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Interaction Energies and NMR Indirect Nuclear Spin−Spin Coupling Constants in Linear HCN and HNC Complexes

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The cooperativity effects on both the electronic energy and NMR indirect nuclear spin−spin coupling constants J of the linear complexes $(HCN)_n$ and $(HNC)_n$ ($n = 1-6$) are discussed. The geometries of the complexes were optimized at the MP2 level by using the cc-pVTZ basis sets. The spin−spin coupling constants were calculated at the level of the second-order polarization propagator approximation with use of the local dense basis set scheme based on the cc-pVTZ-J basis sets. We find strong correlations in the patterns of different properties such as interaction energy, hydrogen bond distances, and spin−spin coupling constants for both series of compounds. The intramolecular spin−spin couplings are with two exceptions dominated by the Fermi contact (FC) mechanism, while the FC term is the only nonvanishing contribution for the intermolecular couplings. The latter do not follow the Dirac vector model and are important only between nearest neighbors.

1. Introduction

The cooperativity or nonadditive effects on electronic energies in hydrogen bond (HB) clusters can be defined as the difference between the total interaction energy of an aggregation of molecules and the sum of the pair-wise interaction energies. A number of other molecular properties (e.g., geometry, dipole moment, and molecular stretching frequencies) are affected by cooperativity effects. As an example, cooperativity effects in water increase significantly its basicity and thus a water trimer is comparable to ammonia.[1] In recent years an ever increasing number of theoretical studies have been devoted to study the cooperativity effects in HB systems.[2−5]

The application of indirect nuclear spin−spin coupling constants, J, for the analysis of hydrogen bonded complexes has become an emerging area of research since the experimental observation of measurable J values in bis-iminophosphoranes.[6] The great advantage of using J-coupling constants in the determination of structures and conformational constraints of chemical compounds is due to their strong sensitivity to structural changes.[7] Significant progress has also been made in the understanding of the vibrational effects on NMR properties of hydrogen bonded complexes.[8] It was demonstrated that the environment also influences these properties which, at the same time, provide important information about the structure of the hydrogen bond.[9]

Linear chains of $(HCN)_n$ and $(HNC)_n$ have recently been studied as model compounds for analyzing cooperativity effects on bond lengths in complexes.[10−12] King et al.[10] have shown with an NBO analysis that an electronic mechanism causes such an effect on bond lengths. Experimentally, linear chains of hydrogen cyanide embedded in supercritical helium have been studied in the gas phase showing a variation of the free CH stretching frequency with the size of the chain.[13]

The experimental work of Juranic and Macura[14] suggested that the correlation with a negative slope between two different J-couplings in the same complex, an intramolecular and an intermolecular coupling which include the same common nucleus, is due to the competition between the intermolecular (DH) and the intramolecular bond (HA) in D−H···A. A positive slope is interpreted as due to the enhancement of the HB's in the complex leading to a positive cooperativity. For instance, the competition between the amide HB and the peptide bond for the s-electron density of the nitrogen in an amide chain is observed as the negative slope between the intramolecular $^{1}J(N,C)$ and the intermolecular $^{HB+2}J(N,C)$. In line with this, the comparison of equivalent coupling constants in HCN and HNC series of model compounds will show which relation exists between them and therefore also whether the two series of compounds exhibit any similarities.

In the present article, linear chains of $(HCN)_n$ and $(HNC)_n$ ($n = 1-6$) have been studied as general models of linear hydrogen-bonded clusters. Interaction energy and spin−spin coupling constant correlations and cooperativity effects were investigated. Correlations between intramolecular couplings in the two series as well as those between the intra- and intermolecular couplings have been analyzed.

This paper is organized in the following way: section 2 describes the method used for the optimization of the geometries and the calculation of the spin−spin coupling constants. The results are discussed in section 3. Finally, in section 4, the most important conclusions are summarized.

2. Method of Calculation

The geometry of all molecular complexes has been optimized with the Gaussian-98 program[15] at the MP2 level[16] using the cc-pVTZ basis sets[17] with frozen core approximation. In all cases $C_{\infty v}$ symmetry has been adopted. The numbering of the

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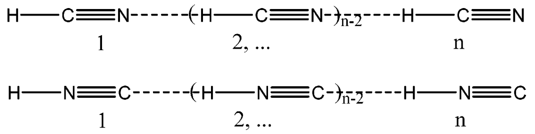
CHART 1: Labeling of the Molecules in the Two Series of Complexes



$$\underset{1}{\mathrm{H{-}C{\equiv}N}}\cdots\cdots(\underset{2,\ldots}{\mathrm{H{-}C{\equiv}N}}\cdots)_{n-2}\cdots\underset{n}{\mathrm{H{-}C{\equiv}N}}$$

$$\underset{1}{\mathrm{H{-}N{\equiv}C}}\cdots\cdots(\underset{2,\ldots}{\mathrm{H{-}N{\equiv}C}}\cdots)_{n-2}\cdots\underset{n}{\mathrm{H{-}N{\equiv}C}}$$

TABLE 1: Bond Lengths (in Å) of the Molecular Clusters Calculated at the MP2/cc-pVTZ Frozen Core Level

	$(HCN)_n$			$(HNC)_n$		
cluster size n (position in chain)	R(HC)	R(CN)	HB length[a]	R(HN)	R(NC)	HB length[a]
1 (1)	1.064	1.167		0.996	1.176	
2 (1)	1.065	1.165		0.998	1.171	
2 (2)	1.071	1.167	2.197	1.013	1.176	2.051
3 (1)	1.066	1.165		0.998	1.170	
3 (2)	1.073	1.165	2.145	1.020	1.170	1.979
3 (3)	1.073	1.167	2.153	1.018	1.175	1.996
4 (1)	1.066	1.165		0.999	1.169	
4 (2)	1.074	1.165	2.132	1.023	1.169	1.957
4 (3)	1.076	1.166	2.096	1.028	1.171	1.915
4 (4)	1.073	1.167	2.143	1.020	1.176	1.979
5 (1)	1.066	1.165		0.999	1.169	
5 (2)	1.074	1.165	2.126	1.024	1.169	1.947
5 (3)	1.076	1.165	2.084	1.032	1.169	1.891
5 (4)	1.076	1.165	2.084	1.031	1.170	1.894
5 (5)	1.073	1.167	2.137	1.021	1.176	1.972
6 (1)	1.066	1.165		0.999	1.169	
6 (2)	1.075	1.165	2.123	1.025	1.169	1.942
6 (3)	1.077	1.165	2.077	1.034	1.169	1.880
6 (4)	1.077	1.165	2.070	1.035	1.169	1.869
6 (5)	1.077	1.165	2.078	1.033	1.170	1.885
6 (6)	1.074	1.167	2.136	1.022	1.176	1.968

[a] It corresponds to the H-bond to the preceding molecule.

molecules within the complexes is shown in Chart 1. The geometrical parameters of the studied molecular chains are collected in Table 1.

The interaction energy has been calculated as the difference of the energy of the whole complex and the sum of the energies of the corresponding noninteracting molecules. The BSSE error calculated for the dimers is 0.51 and 0.58 kcal/mol for the $(HCN)_2$ and $(HNC)_2$ complexes, respectively. Because of the small values obtained for this correction and previous reports in the literature,[18] it has not been considered for the rest of the complexes. Other potential corrections to the interaction energy as the distortion energy of the monomers have been calculated for the dimers obtaining very small values (0.02 and 0.19 kcal/mol for the $(HCN)_2$ and $(HNC)_2$ complexes, respectively).

The four different Ramsey contributions[19] to the indirect spin−spin coupling constants, i.e., Fermi contact (FC), spin dipolar (SD), paramagnetic spin−orbital (PSO), and diamagnetic spin−orbital (DSO), account for two transmission mechanisms of the spin interaction: (a) the interaction between nuclear and electron spins and (b) the interaction between nuclear spins and the orbital angular momentum of the electrons. The former is accounted for by the FC and the SD contributions, whereas the latter is given by the PSO and DSO contributions.

All coupling constants were calculated with the second-order polarization propagator approximation (SOPPA),[20−22] which is based on second-order Møller−Plesset (MP2) perturbation theory.[16] Electron correlation effects are thus accounted for through second order in the fluctuation potential. SOPPA was often shown to give very reliable one-bond and long-range spin−spin coupling constants not only in small molecules[21−30] but also in a wide range of hydrocarbons.[31] The SOPPA calculations were performed with the Dalton 1.2 program package.[32]

A recently developed locally dense basis sets (LDBS) scheme[29,33] was employed to keep the size of the basis set within the current limitations of the SOPPA implementation in the DALTON program. For nuclei in the coupling pathway which are considered to be important the cc-pVTZ-J[30,34] basis set was used. This basis set permits an adequate treatment of the cusp of the wave function at the nucleus and therefore gives a very good description of the FC term [ref 30 and references therein]. For all other atoms a smaller basis set was employed, following a criterion that was successfully applied in other compounds.[29,33,35] In the present study the LDBS scheme consists of the following: (a) for calculations of intramolecular couplings the cc-pVTZ-J[30,34] basis set was employed on all atoms belonging to the molecule in the chain, which includes the coupled atoms, whereas the cc-pVDZ basis set[17] was used for all other atoms; (b) and for calculations of intermolecular couplings the cc-pVTZ-J basis set was again used for all atoms of the two molecules in the chain which include the coupled atoms and the cc-pVDZ basis set for all other atoms.

3. Results and Discussions

3.1. Electronic Energies. The total electronic energy, E_{total}, and the interaction energy, E_{I}, of the complexes are collected in Table 2. For both types of complexes the total energies agree quite well with the results obtained by Chen et al.[11] at the DFT-B3LYP/6-311+G(2d,p) level. The interaction energies are slightly smaller than the ones obtained by Rivelino et al. at the MP2/6-311++G(d,p) level.[12]

A measure of the cooperativity effect consists of the difference in interaction energies between a given chain and the same chain without one of the interacting molecules. When cooperativity effects are involved the value of the electronic interaction energy for a cluster with n units should increase in absolute value more than the sum of the electronic energy of the previous cluster with $n - 1$ units and the electronic energy of the added monomer. As observed in Figure 1, the E_{I} values in $(HNC)_n$ for the new hydrogen bonds increase in absolute value up to 45% in the last HB of the hexamer when compared to the E_{I} obtained in the dimer.

Cooperativity effects are larger for the $(HNC)_n$ clusters. This difference in E_{I} could be due to the fact that HB distances are smaller in the (HNC) clusters than in the $(HCN)_n$ clusters. As shown in Figure 2, an exact linear correlation is obtained when the interaction energies of both clusters, $(HCN)_n$ and $(HNC)_n$, for the same value of n are compared. This indicates a very similar behavior of the two electronic systems, though the slope shows which complex has the largest cooperative effect.

3.2. Bond Lengths. The experimental bond lengths in HCN are $r_{(\mathrm{CN})} = 1.153$ Å and $r_{(\mathrm{CH})} = 1.065$ Å, respectively. The results of our calculations, see Table 1, are therefore closer to the experimental values than the bond lengths obtained by King and Weinhold [10] and Kofranek et al.[36] However, the experimental hydrogen bond length in the HCN dimer, $r_{(\mathrm{N\cdots H})} = 2.229$ Å,[37] was better reproduced by Chen et al.[11] at the DFT level. In general our MP2 calculations, see Table 1, give shorter bond lengths for $r_{(\mathrm{CH})}$ and $r_{(\mathrm{N\cdots H})}$ in $(HCN)_n$ as well as $r_{(\mathrm{NH})}$ and $r_{(\mathrm{N\cdots H})}$ in $(HNC)_n$ than the DFT calculations of Chen et al.[11]

As previously observed,[10−12] the effects of the HB on the geometrical parameters of the individual molecules are the enlargement of the donor H-bond (HC and HN) and the shortening of the involved bonds in the H-bond acceptor (CN

TABLE 2: Total Electronic Energy, E_{total} (in hartrees), and Electronic Interaction Energy, E_I (in kcal/mol), of the Molecular Chains Calculated at the MP2/cc-pVTZ Level without Counterpoise Correction

compd	E_{total}	E_I this work	E_I RCC[a]	compd	E_{total}	E_I
HCN	−93.25359			HNC	−93.22497	
$(HCN)_2$	−186.51514	−4.99	−4.66	$(HNC)_2$	−186.46282	−8.08
$(HCN)_3$	−279.77847	−11.11	−10.34	$(HNC)_3$	−279.70422	−18.39
$(HCN)_4$	−373.04242	−17.61	−16.35	$(HNC)_4$	−372.94698	−29.55
$(HCN)_5$	−466.30663	−24.27	−22.51	$(HNC)_5$	−466.19036	−41.10
$(HCN)_6$	−559.57096	−31.01	−28.74	$(HNC)_6$	−559.43405	−52.85

[a] MP2/6-311++G(d,p) calculation by Rivelino, Chaudhuri, and Canuto.[12]

and NC). Cooperativity effects are clearly observed in the length of all hydrogen bonds which are shortened as the size of the cluster increases (Table 1). This is especially the case for the H bond located at the center of the chain. Comparison of the 15 comparable intermolecular distances in the two series of chains exposes a very good linear correlation, $R_{(HB)}(HNC)_n = 1.4316R_{(HB)}(HCN)_n - 1.0916$ with an R^2 value of 0.995.

3.3. Intramolecular Nuclear Spin−Spin Couplings. All of the intramolecular coupling constants are shown in Table 3. The effect of the other molecules in a chain on a given intramolecular *J*-coupling is an increase in the absolute value. In analogy with the cooperativity effect on HB lengths, this increase in the coupling constants can be considered as the corresponding cooperativity effect on the couplings. The amount of this change converges to a constant value as the size of the chain increases. If one compares a particular coupling constant $^mJ(X,Y)$ ($m = 1$ or 2) in the first unit of the chain, i.e., unit 1 according to our nomenclature as shown in Chart 1, for a chain with *i* units and for a chain with one more unit, one notes that the increase in this coupling, $\Delta^mJ(X,Y)_{i+1,i}$, monotonically diminishes with the size *i* of the chain and is constant for $i \geq 3$. The changes in the $^1J(C,N)$ coupling in the $(HCN)_n$ series are, e.g., $\Delta^1J(C,N)_{2,1} = 2.9$ Hz, $\Delta^1J(C,N)_{3,2} = 0.6$ Hz, $\Delta^1J(C,N)_{4,3} = 0.2$ Hz, and $\Delta^1J(C,N)_{5,4} = 0.1$ Hz. This pattern holds for all intramolecular couplings.

TABLE 3: Total Intramolecular Coupling Constants (in Hz)

cluster size *n* (position in chain)	$(HCN)_n$ $^1J(C,H)$	$(HCN)_n$ $^1J(C,N)$	$(HCN)_n$ $^2J(N,H)$	$(HNC)_n$ $^1J(N,H)$	$(HNC)_n$ $^1J(N,C)$	$(HNC)_n$ $^2J(C,H)$
1	275.3	−12.9	−7.0	−126.3	−5.6	21.2
2 (1)	281.5	−15.8	−8.0	−130.2	−11.1	24.9
2 (2)	277.9	−13.6	−8.1	−124.4	−7.0	23.6
3 (1)	282.9	−16.4	−8.2	−131.2	−12.4	25.8
3 (2)	283.7	−16.3	−9.1	−126.4	−12.1	27.1
3 (3)	278.3	−13.7	−8.3	−123.6	−7.2	24.0
4 (1)	283.4	−16.6	−8.3	−131.5	−12.9	26.1
4 (2)	284.8	−16.9	−9.3	−126.7	−13.3	28.0
4 (3)	283.7	−16.3	−9.3	−124.6	−12.1	27.3
4 (4)	278.3	−13.7	−8.3	−123.1	−7.3	24.1
5 (1)	283.6	−16.7	−8.3	−131.7	−13.1	26.3
5 (2)	285.2	−17.0	−9.4	−126.7	−13.7	28.3
5 (3)	284.9	−16.9	−9.6	−124.5	−13.3	28.1
5 (4)	283.7	−16.4	−9.4	−123.8	−12.1	27.4
5 (5)	278.3	−13.8	−8.4	−122.9	−7.3	24.1

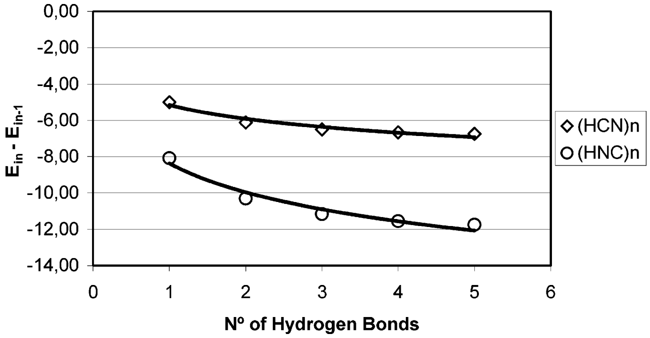


Figure 1. Increase of the interaction energy E_I vs the number of hydrogen bonds. Adjusted curves: for the $(HNC)_n$ cluster, $(E_{In} - E_{In-1}) = -2.3045\ \ln(\text{no. of H bonds}) - 8.364$ with $R^2 = 0.9582$; and for the $(HCN)_n$ clusters, $(E_{In} - E_{In-1}) = -1.0966\ \ln(\text{no. of H bonds}) - 5.1528$ with $R^2 = 0.94$.

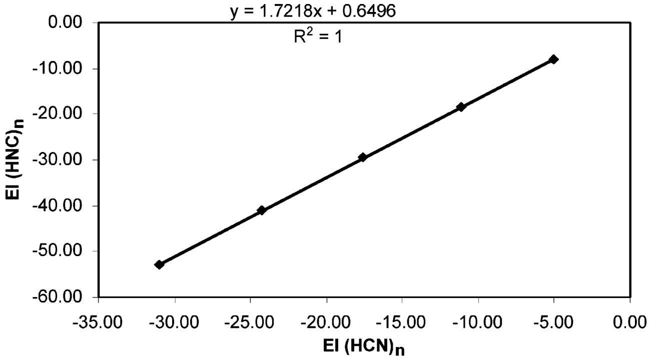


Figure 2. Interaction energy E_I of $(HCN)_n$ (kcal mol^{-1}) versus E_I of $(HNC)_n$ (kcal mol^{-1}). The corresponding linear regression is shown in the figure.

In all cases but the $^1J(N,H)$ couplings in $(HNC)_n$, the absolute values of the intramolecular couplings are larger in the cluster than in the monomers. There are some differences in the intramolecular couplings in both series of chains. In the case of the CN couplings the changes are more pronounced in the $(HNC)_n$ chains than in the $(HCN)_n$ chains. The difference between that coupling in the monomer and its value in the dimer is more than 50% of the monomer value for $(HNC)_n$, whereas the difference is less than 20% in the $(HCN)_n$ chain. This fact may reflect a larger sensitivity of the HNC moiety as HB acceptor compared with the HCN moiety.

Another remarkable difference is observed between the CH and NH couplings. The $^1J(N,H)$ always has the largest absolute value in a given complex for the NH bond not involved in a hydrogen bond, whereas the maximum value of the $^1J(C,H)$ couplings always is reached in the second molecule in the chain, i.e. the first molecule involved in a hydrogen bond (see Figures 5 and 6). Furthermore, the absolute value of the NH couplings is smaller in the last few units in the oligomers than in the monomer but increases within the chain and becomes larger than in the monomer again for the first molecule in the cluster that acts as a hydrogen bond donor. In case of the NH couplings a lengthening of the hydrogen bond−donor bond, N−H, within a cluster leads thus to an increase of the absolute value of its coupling constant, whereas the lengthening of corresponding hydrogen bond−donor bonds in different clusters leads to a decrease in the absolute value of their couplings, as one might have expected.[25,38] However, in case of the CH couplings a lengthening of the hydrogen bond donor bond, C−H, always yields a larger $^1J(C,H)$ coupling.

TABLE 4: The Four Ramsey Contributions to the Intramolecular Coupling Constants (in Hz) in the Monomer and the Trimer of the Complex (HCN)$_n$

coupling	cluster size *n* (position in chain)	J^{DSO}	J^{PSO}	J^{SD}	J^{FC}	J
^1J(N,C)	1 (1)	0.03	0.42	−4.82	−8.55	−12.91
	3 (1)	0.03	0.12	−4.89	−11.70	−16.44
	3 (2)	0.03	0.63	−4.72	−12.20	−16.27
	3 (3)	0.03	0.94	−4.64	−10.03	−13.70
^1J(C,H)	1 (1)	0.36	−0.48	0.52	274.91	275.31
	3 (1)	0.36	−0.59	0.58	282.57	282.93
	3 (2)	0.46	−0.72	0.68	283.28	283.70
	3 (3)	0.46	−0.66	0.63	277.87	278.29
^2J(N,H)	1 (1)	0.61	−3.49	−0.70	−3.46	−7.05
	3 (1)	0.60	−3.47	−0.68	−4.64	−8.19
	3 (2)	0.57	−3.50	−0.75	−5.43	−9.10
	3 (3)	0.58	−3.53	−0.77	−4.56	−8.28

Even though the FC term gives the most important contribution to the total coupling constant for all but two couplings, the percentage depends strongly on the type of coupling and the size of the cluster as illustrated for the monomer and trimer in Tables 4 and 5. In case of the two one-bond couplings to a hydrogen atom, ^1J(C,H) and ^1J(N,H), the FC term is the only important contribution. On the other hand, for ^1J(C,N) the SD contribution is about 40−65% of the FC term with the exception of the HNC monomer, where the SD contribution is about a factor of 1.3 times larger than the FC term and therefore the largest contribution to this coupling. In the last case the FC contribution diminishes drastically compared with its value in the corresponding (HCN)$_n$ complex. In general, the noncontact contributions to the ^1J(C,N) couplings are larger in percentage of the FC term in the (HNC)$_n$ chains than in (HCN)$_n$ analogues. The geminal couplings, ^2J(C,H) and ^2J(N,H), finally have large PSO contributions which are about 40% of the FC term for the ^2J(C,H) coupling and about 70% for the ^2J(N,H) coupling with the exception of the coupling in HCN where the PSO term is actually slightly larger than the FC term.

In both monomers we thus find that the SD and FC contributions to ^1J(C,N) or ^1J(N,C) are much larger than the PSO terms. This is in contrast to what was found for comparable couplings in similar systems such as N_2 and CO[17,23,39] or $H_2C{=}NH$.[20] In the also triply bonded systems N_2 and CO the PSO term is by far the largest contribution, whereas in $H_2C{=}NH$ the PSO term still amounts to about 80% of the FC term and the SD term is on the order of 10% of the FC term.

In the following, the trends in the four contributions to the one- and two-bond couplings as a function of the cluster size are discussed in more detail.

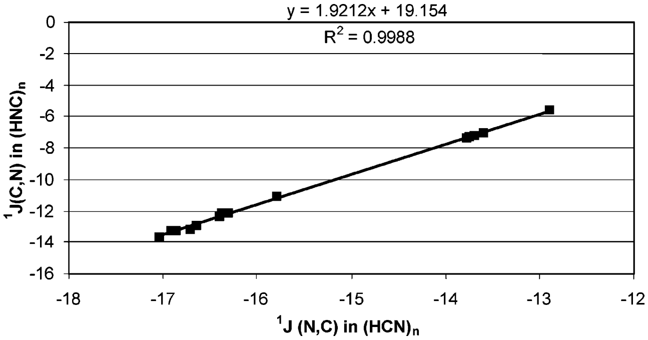


Figure 3. Correlation between ^1J(C,N) in (HCN)$_n$ and ^1J(N,C) in (HNC)$_n$.

3.3.1. One-Bond Couplings. Figure 3 shows that the correlation between the ^1J(C,N) couplings in the (HCN)$_n$ series and the ^1J(N,C) couplings in the (HNC)$_n$ series is close to one. This means that the two series of complexes exhibit a similar behavior with respect to the cooperativity effects on this coupling constant. In the rest of this section we will therefore only analyze the changes in the contributions to the ^1J(C,N) couplings in the (HCN)$_n$ series.

In Figure 4 the individual contributions to the ^1J(C,N) couplings in (HCN)$_n$ are shown as a function of the size *n* of the chain and the position in the complex. The absolute value of the FC contribution (Figure 4c) for a given position in the chain increases systematically with the size of the complex, whereas the largest FC contribution to this coupling is always observed for the unit in the middle of the chain similar to the geometrical effect discussed previously in section 3.2.

The PSO and SD contributions (see Figure 4a and 4b), on the other hand, exhibit quite a different pattern. The absolute value of the PSO term for the same element in the chain increases with the size of the complex whereas the absolute value of the negative SD contribution decreases slowly. However, this increase dies off quickly with the size of the chain. The largest difference in both contributions is thus observed between the monomer and the dimer and we expect the values for the pentamer to be close to the infinite chain limit. Both terms vary almost linearly with respect to the position of the coupled nuclei in the chain with no sign of saturation. Starting with the tetramer we observe a marked border effect, which means that the differences between the couplings in the two terminal units and the couplings in the inner units of the chain are much larger than the differences between the inner units themselves. The change in the SD term between the two terminal units is about 0.3 Hz, whereas for the PSO term the variation spans about 1.0 Hz for (HCN)$_n$ and about 1.5 Hz for (HNC)$_n$ (with $n = 2, ..., 5$). The total coupling constant ^1J(C,N) (Figure 4d) shows a similar behavior as the FC term but with a slightly smaller variation due to the linear behavior of the PSO and SD

TABLE 5: The Four Ramsey Contributions to the Intramolecular Coupling Constants (in Hz) in the Monomer and the Trimer of the Complex (HNC)$_n$

coupling	cluster size *n* (position in chain)	J^{DSO}	J^{PSO}	J^{SD}	J^{FC}	J
^1J(C,N)	1 (1)	0.02	0.67	−3.50	−2.75	−5.55
	3 (1)	0.02	0.12	−3.86	−8.71	−12.43
	3 (2)	0.02	0.89	−3.71	−9.27	−12.07
	3 (3)	0.02	1.41	−3.42	−5.23	−7.22
^1J(N,H)	1 (1)	−0.17	−0.57	−0.29	−125.28	−126.32
	3 (1)	−0.17	−0.34	−0.31	−130.34	−131.17
	3 (2)	−0.22	0.07	−0.33	−125.91	−126.38
	3 (3)	−0.22	−0.03	−0.30	−123.00	−123.55
^2J(C,H)	1 (1)	−2.01	6.56	0.91	15.76	21.22
	3 (1)	−1.99	6.77	0.94	20.08	25.80
	3 (2)	−1.84	6.96	1.12	20.86	27.10
	3 (3)	−1.86	6.87	1.13	17.83	23.98

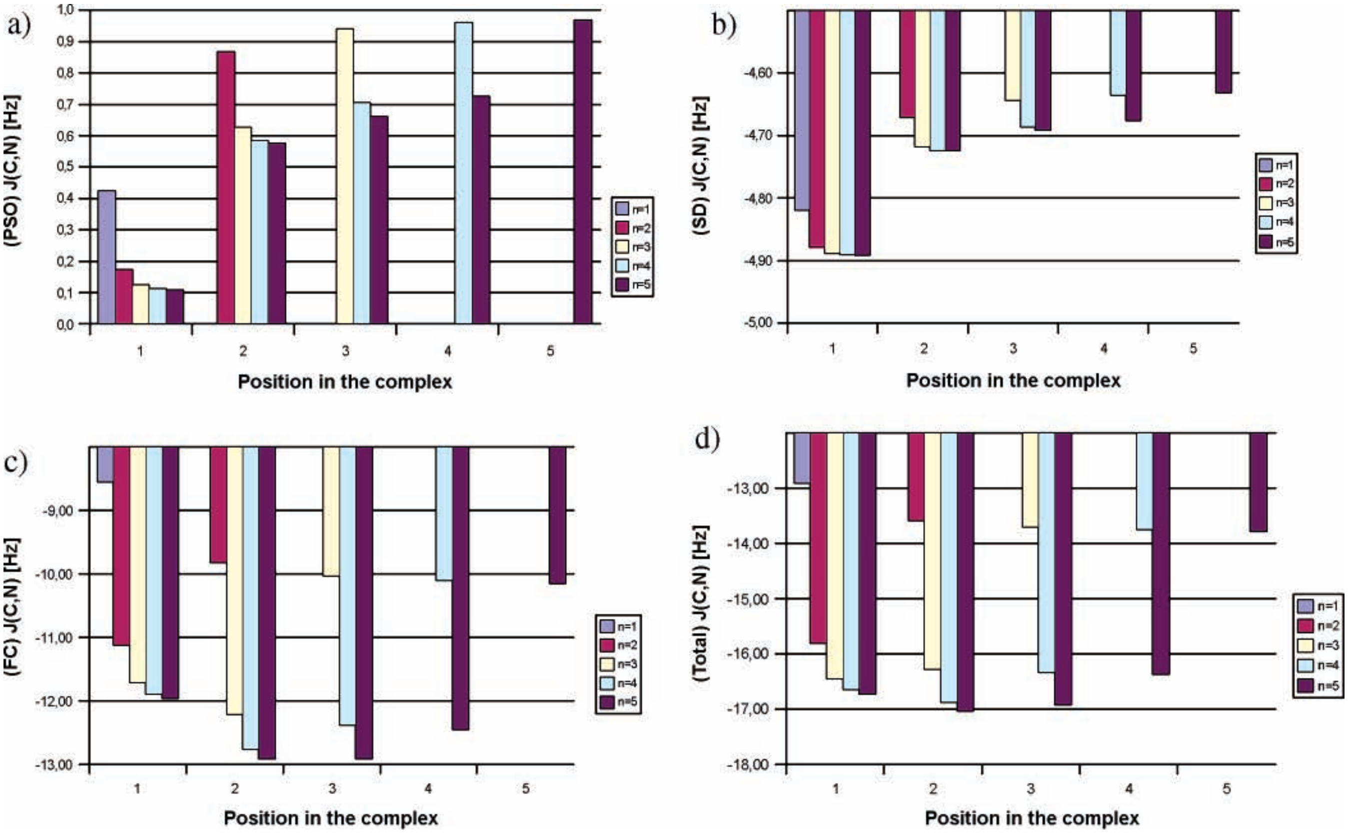


Figure 4. Intramolecular ^1J(C,N) coupling in $(\mathrm{HCN})_n$ as a function of both the size n of the complex and the position in the complex: (a) PSO contribution; (b) SD contribution; (c) FC contribution; and (d) total coupling.

contributions. This linear behavior may be more pronounced for larger clusters and thus could lead to an observable effect in the total coupling constant. The DSO term finally is positive and almost negligible and its variation with cluster size and position in the chain is similar to the changes in the total coupling constant.

Turning now to the two one-bond couplings involving hydrogen, ^1J(C,H) and ^1J(N,H), we will use the reduced coupling constant K defined as

$$K(\mathrm{M,N}) = \frac{4\pi^2}{\hbar\gamma_\mathrm{M}\gamma_\mathrm{N}} J(\mathrm{M,N})$$

because it is independent of the gyromagnetic ratios, γ_M, of the coupled nuclei, and changes in the reduced coupling constant from one pair of nuclei to another therefore reflect only the changes in the electronic structure. The units of the reduced coupling constant are 10^{-20} T^2 J^{-1}.

The ^1K(C,H) couplings for $(\mathrm{NCH})_n$, Figure 5, go through a maximum for the units in the middle of the chain similar to the geometrical effect (section 3.1).

The total ^1K(N,H) couplings in $(\mathrm{HNC})_n$, which are dominated by the FC contribution, exhibit a linear dependence on the position in the chain (see Figure 6b). This linear behavior may be used to distinguish between different units in the complexes. The other contributions show the usual pattern with a maximum for the intermediate units in the chain with the exception of the PSO term, which has a minimum and even changes it sign (see Figure 6a), as in the case of ^1K(C,H). Although the variation of the PSO contribution with the position in the chain is only about 0.5 Hz, it is quite extraordinary.

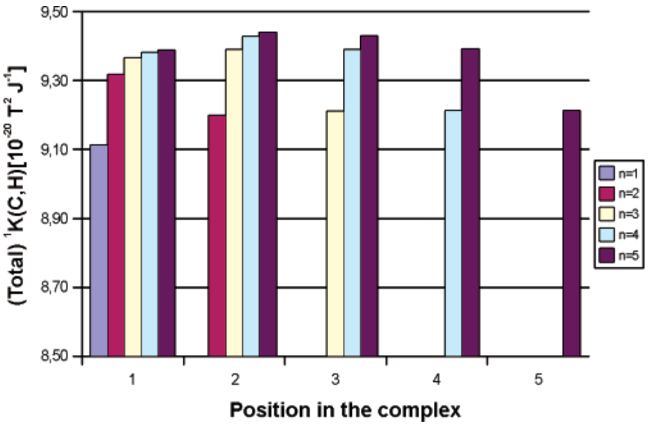


Figure 5. Intramolecular reduced one-bond coupling constant ^1K(C,H) (in units of [10^{-20} T^2 J^{-1}]) for $(\mathrm{HCN})_n$ as a function of both the size n of the complex and the position in the complex.

3.3.2. Two-Bond Couplings. In this section we analyze the reduced coupling constants ^2K(N,H) for $(\mathrm{HCN})_n$ complexes and ^2K(C,H) for $(\mathrm{HNC})_n$ complexes. Both couplings show similar patterns for their contributions and we discuss therefore only ^2K(N,H). However, one should note that the PSO term is of the same sign and approximately of the same order of magnitude as the FC term in the $(\mathrm{HCN})_n$ case, whereas it is only one-third of the FC term in the $(\mathrm{HNC})_n$ series.

The reduced couplings ^2K(N,H) for $(\mathrm{HCN})_n$ are shown in Figure 7b. The previously observed pattern for the one-bond couplings with a maximum value for the intermediate units and an increase with the size of the chain is again observed here. This pattern is similar to that of the FC term, which is the main contribution of this geminal coupling, whereas the PSO term (see Figure 7a), which is similar in size to the FC term, remains almost unchanged for all units in a given complex. The other two contributions, the DSO and SD terms, are much smaller and almost cancel each other.

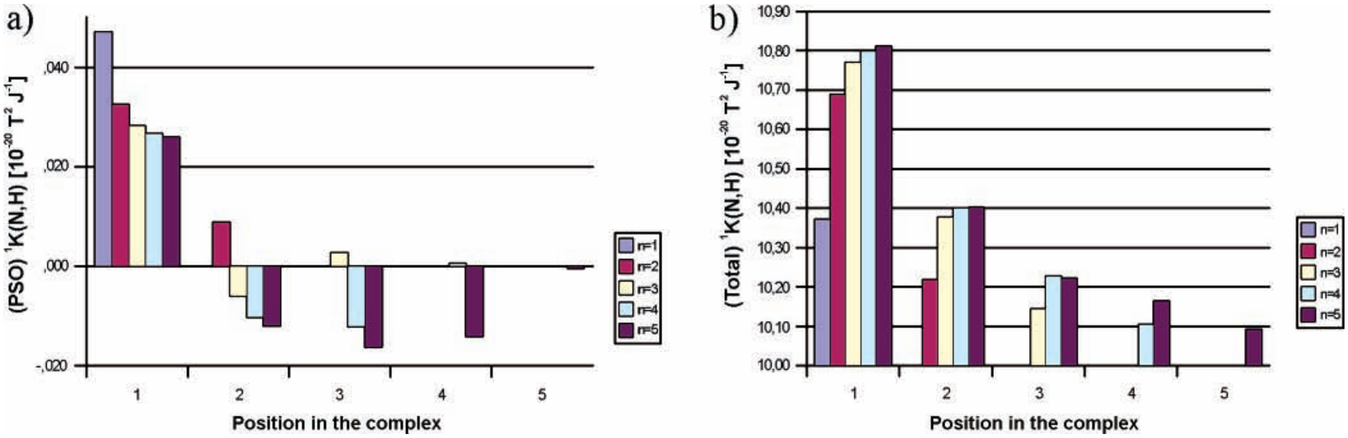


Figure 6. Intramolecular reduced one bond coupling constant ^1K(N,H) (in units of [10^{-20} T^2 J^{-1}]) for $(HNC)_n$ as a function of both the size n of the complex and the position in the complex: (a) PSO contribution and (b) total coupling constant.

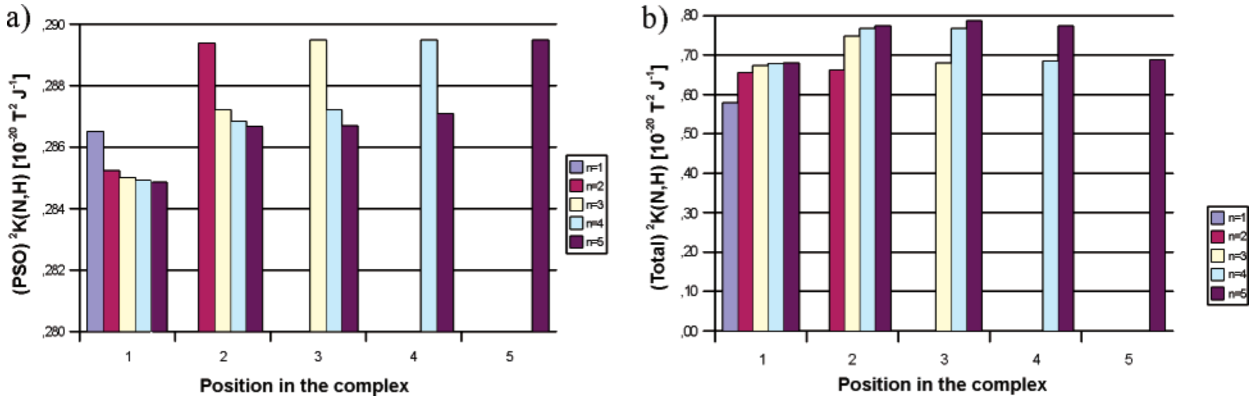


Figure 7. Intramolecular reduced two-bond coupling constant ^2K(N,H) (in units of [10^{-20} T^2 J^{-1}]) for $(HCN)_n$ as a function of both the size *n* of the complex and the position in the complex: (a) PSO contribution and (b) total coupling constant.

TABLE 6: A Selection of the Intermolecular Coupling Constants (in Hz) [Reduced Coupling Constant (in 10^{-20} T^2 J^{-1})] in $(HCN)_n$ Chains[a,b]

cluster size *n* (positions in chain)	$^{1h}J(N_{(i+1)},H_{(i)})$; $^{1h}K(N_{(i+1)},H_{(i)})$	$^{2h}J(N_{(i+1)},C_{(i)})$; $^{2h}K(N_{(i+1)},C_{(i)})$	$^{3h}J(C_{(i+1)},C_{(i)})$; $^{3h}K(C_{(i+1)},C_{(i)})$
2 (1−2)	3.2; −0.266	−8.1; 2.641	2.5; 0.324
3 (1−2)	3.0; −0.246	−9.6; 3.148	2.9; 0.385
3 (2−3)	3.0; −0.243	−9.4; 3.072	2.8; 0.363
4 (1−2)	3.1; −0.252	−10.1; 3.309	3.1; 0.405
4 (2−3)	3.4; −0.283	−11.4; 3.711	3.3; 0.438
4 (1−2)	3.0; −0.248	−9.8; 3.195	2.9; 0.375

[a] Only couplings which are larger than 1 Hz are shown. [b] The "h" as part of the superscript on the left of "*J*" indicates that the coupling constant is occurring through a hydrogen bond, while the number has the usual meaning.

3.4. Intermolecular Couplings. A selection of the nonnegligible intermolecular coupling constants are gathered in Tables 6 and 7 (a complete list is included in the Supporting Information). The FC term is by far the most important contribution to all couplings shown in Tables 6 and 7.

Linear correlations between the two series are found for the $N_{(i+1)}-C_{(i)}$ couplings, $^{2h}J(N_{(i+1)},C_{(i)})_{(NCH)_n} = 2.559 \times {}^{2h}J(C_{(i+1)},N_{(i)})_{(CNH)_n} + 4.4424$ with $R^2 = 0.9828$, and the $C_{(i+1)}-C_{(i)}$ couplings, $^{2h}J(C_{(i+1)},C_{(i)})_{(NCH)_n} = 2.1256 \times {}^{2h}J(C_{(i+1)},C_{(i)})_{(CNH)_n} + 3.7694$ with $R^2 = 0.9817$.

However, we could not find any correlation between the HB distance and ^{HB}J.

All nonnegligible intermolecular one- and two-bond coupling constants have a FC term that fails to follow the Dirac vector model. Thus, for the across-HB coupling pathway, i.e., for $^{1h}K^{FC}(N_{(i+1)},H_{(i)})$ and $^{1h}K^{FC}(C_{(i+1)},H_{(i)})$ in Figures 8a and 9a, the FC term is negative, whereas for all the other coupling constants which include one or more covalent bonds in their coupling pathways the FC terms are positive, see Figures 8b,c and 9b,c,d. This fact may suggest, although not conclusively,[40] that the transmission of ^{1h}J(H,Acceptor) couplings through the HB's in

TABLE 7: A Selection of the Intermolecular Coupling Constants [Reduced Coupling Constant (in 10^{-20} T^2 J^{-1})] in $(HNC)_n$ Chains (in Hz)[a,b]

cluster size *n* (positions in chain)	$^{1h}J(C_{(i+1)},H_{(i)})$; $^{1h}K(C_{(i+1)},H_{(i)})$	$^{2h}J(C_{(i+1)},N_{(i)})$; $^{2h}K(C_{(i+1)},N_{(i)})$	$^{3h}J(N_{(i+1)},N_{(i)})$; $^{3h}K(N_{(i+1)},N_{(i)})$	$^{3h}J(C_{(i+1)},C_{(i)})$; $^{3h}K(C_{(i+1)},C_{(i)})$
2 (1−2)	−5.5; −0.184	−16.3; 5.333	1.2; 0.948	1.5; 0.200
3 (1−2)	−5.1; −0.170	−20.5; 6.704	1.5; 1.206	2.5; 0.331
3 (2−3)	−5.3; −0.176	−19.2; 6.270	1.3; 1.058	2.0; 0.263
4 (1−2)	−4.8; −0.158	−22.0; 7.183	1.6; 1.292	2.9; 0.377
4 (2−3)	−4.1; −0.135	−24.5; 8.005	1.7; 1.363	3.3; 0.431
4 (3−4)	−5.3; −0.175	−20.3; 6.624	1.4; 1.103	2.2; 0.287

[b] The "h" as part of the superscript on the left of "*J*" indicates that the coupling constant is occurring through a hydrogen bond, while the number has the usual meaning. [b] Only couplings which are larger than 1 Hz are shown.

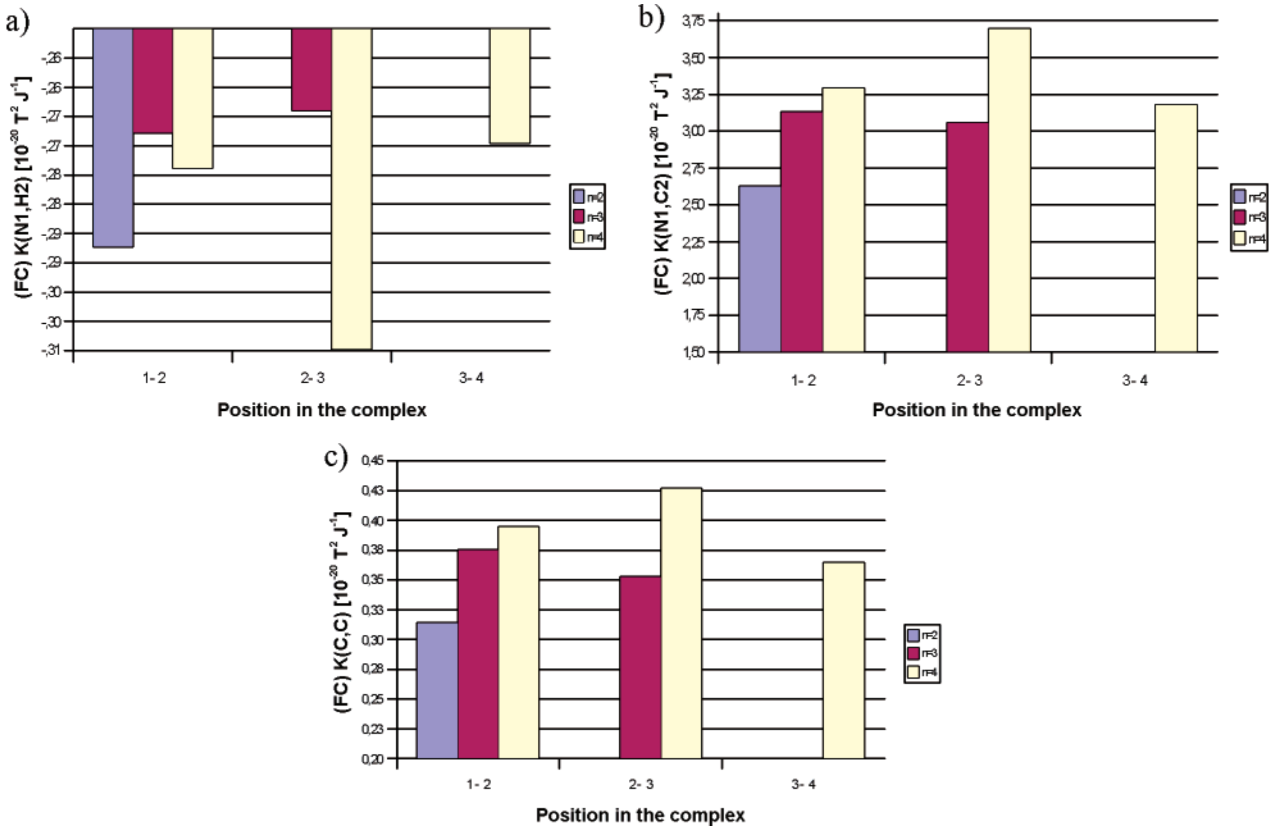


Figure 8. FC contributions to some reduced intermolecular couplings (in units of [10^{-20} T^2 J^{-1}]) in $(HCN)_n$ as a function of both the size n of the complex and the position in the complex: (a) $^{1h}K(N_{(i+1)},H_{(i)})$, (b) $^{2h}K(N_{(i+1)},C_{(i)})$, and (c) $^{3h}K(C_{(i+1)},C_{(i)})$.

the studied chains is mediated by a noncovalent interaction, which may arise from the mutual penetration of the nonbonding van der Waals shells of the involved atoms, in agreement with previous results obtained by Arnold and Oldfield[5] based on the Atoms in Molecules (AIM) model. However, this is in opposition with the explanation given by Cornilescu et al.[3] to the experimental observation of $^{1h}J(N,C)$ through a H bond in ubiquitin.

For the tetramers we find that all FC contributions as well as all total reduced intermolecular couplings have a maximum for the couplings between the two central units with the exception of $^{1h}K(N,H)$ in $(HCN)_4$ where it is a minimum (Figure 8a). Furthermore, up to the tetramer the FC contributions as well as the total couplings increase with the chain length, again with the exception of $^{1h}K(N,H)$ in $(HCN)_n$. The relative large values of $^{2h}K(N_{(i+1)},C_{(i)})$ in $(HCN)_n$ and $^{2h}K(C_{(i+1)},N_{(i)})$ in $(HNC)_n$ and their different magnitude should make it possible to identify the complex and the involved nuclei from measured couplings.

The set of observable intermolecular coupling constants in both series of complexes, i.e., $(HCN)_n$ and $(HNC)_n$, is restricted to the couplings between nearest neighbor units. All couplings between units that are not directly bonded are smaller than 1 Hz, which probably makes it difficult to measure them. This indicates that there is no strong mesomeric effect between the π-orbitals along the complexes and that the transmission of the intermolecular coupling constant occurs mainly through space,[41] i.e., through the overlap of σ-orbitals in the HB pathway, contrary to some coupling constants through C=C moieties.[35,42,43]

Some correlations have been found between the intra- and intermolecular coupling constants involving a common atom. In both series the intramolecular $^1J(N_{(i)},C_{(i)})$ coupling correlates with both the $^{2h}J(N_{(i+1)},C_{(i)})$ and $^{3h}J(C_{(i+1)},C_{(i)})$ couplings (R^2 larger than 0.95 in the four cases). Taking into account the negative value of the gyromagnetic ratio of nitrogen, we find in all cases correlations with positive slopes. This indicates that the formation of the hydrogen bond increases the electron density of the CN moiety within the monomers.[14]

3.5. The Electronic Origin of Intramolecular *J*-Cooperative Effects. Since the series of $(HCN)_n$ complexes is more sensitive to the effects of the hydrogen bonds and otherwise shows a similar behavior as the $(HNC)_n$ complexes, we will concentrate on the first series. From Tables 1 and 3, it can be seen that, even when the H−C bond distances in the monomer and in the first unit of each complex are very similar, i.e., from monomer to pentamer or hexamer it increases only by 0.002 Å, the respective variation in the coupling constants from monomer to pentamer is 8.3 Hz (3%). The same analysis for the monomer and the last unit in each complex shows an increment in the bond distance of 0.01 Å and a corresponding increment in the coupling of 3 Hz (1%). Hence, the couplings seem to be more sensitive to the enlargement of the bond length of the first units of the chains than for the last ones. This fact suggests a mechanism that accounts for the changes on *J* being different than those which arose from geometrical changes.

Furthermore, the C−N bonding distances are almost unchanged along the series of complexes and also within one of them. For instance, for all the last units in the complexes analyzed, the C−N bond distance decreases by only 0.002 Å. However, the coupling constants vary strongly with a maximum change of 4 Hz and a minimum in the coupling constants for the fist (dimer and trimer) or second (tetramer and pentamer) unit in each complex, see Table 3 and Figure 4.

This already indicates that the geometrical changes cannot be the origin of the changes in the coupling constants. Another test for this hypothesis is shown in Table 8, where the coupling

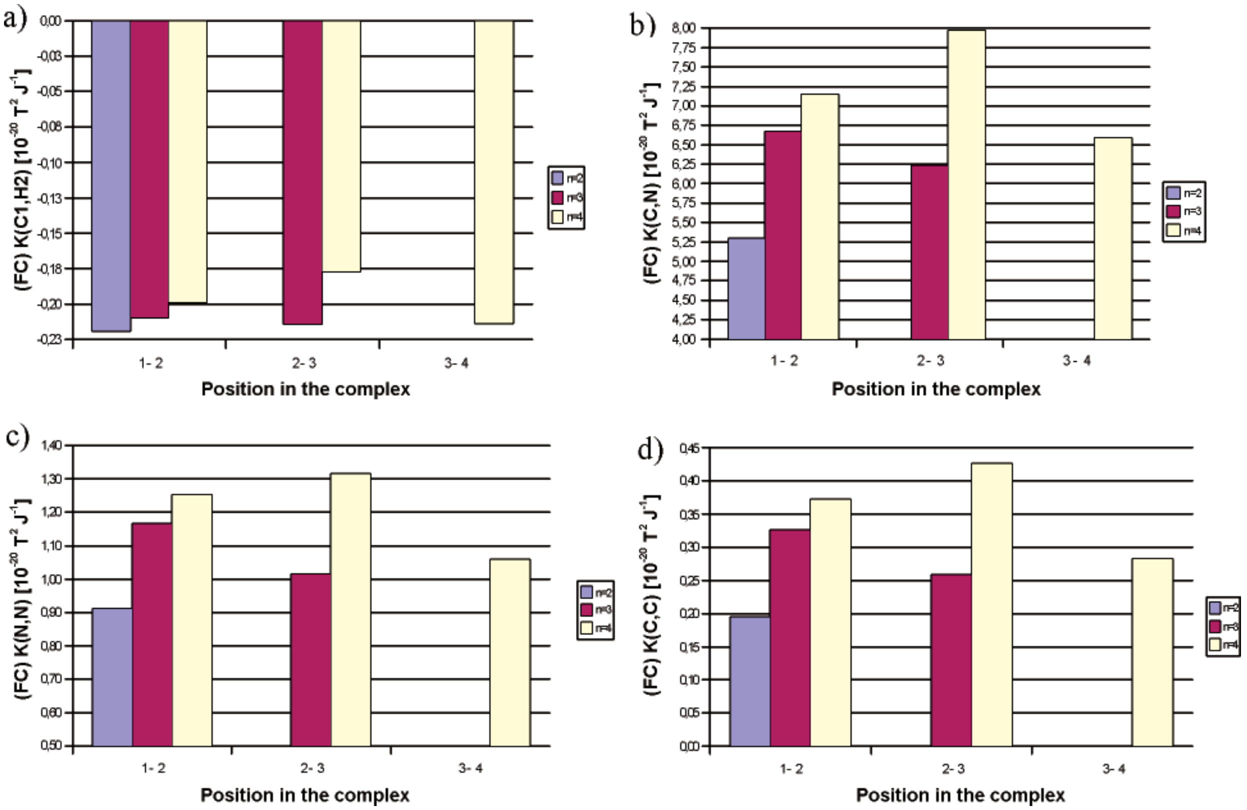


Figure 9. FC contributions to some reduced intermolecular couplings (in units of [10^{-20} T^2 J^{-1}]) in $(HNC)_n$ as a function of both the size n of the complex and the position in the complex: (a) $^{1h}K(C_{(i+1)},H_{(i)})$, (b) $^{2h}K(C_{(i+1)},N_{(i)})$, (c) $^{3h}K(N_{(i+1)},N_{(i)})$, and (d) $^{3h}K(C_{(i+1)},C_{(i)})$.

TABLE 8: Intramolecular Coupling Constants and Their Four Contributions (in Hz) for HCN, for the Geometry of the Central Unit of the $(HCN)_5$ Cluster and for the Central Unit of the $(HCN)_5$ Cluster

cluster size n (positions in chain)	geometry taken from	coupling	J^{DSO}	J^{PSO}	J^{SD}	J^{FC}	J
1 (1)	1 (1)	^1J(C,N)	0.03	0.42	−4.82	−8.55	−12.91
		^1J(C,H)	0.36	−0.48	0.52	274.91	275.31
		^2J(N,H)	0.61	−3.49	−0.70	−3.46	−7.05
1 (1)	5 (3)	^1J(C,N)	0.03	0.37	−4.81	−8.28	−12.69
		^1J(C,H)	0.36	−0.41	0.51	276.89	277.35
		^2J(N,H)	0.60	−3.38	−0.66	−3.41	−6.85
5 (3)	5 (3)	^1J(C,N)	0.02	0.66	−4.69	−12.91	−16.91
		^1J(C,H)	0.47	−0.75	0.73	284.42	284.88
		^2J(N,H)	0.56	−3.49	−0.75	−5.91	−9.59

constants for the monomer, for a monomer with the geometry of the central unit of the $(HCN)_5$ cluster, and for the central unit of the $(HCN)_5$ cluster are shown. We can see that the coupling constants of the monomer with the geometry of the middle unit in the pentamer complex almost coincide with those of the proper monomer, while the couplings in the middle unit of the pentamer are distinctly different. The variation in the intramolecular couplings is thus almost entirely due to an electronic effect and not to the geometrical effect.

Considering also the fact that all intramolecular couplings increase in absolute value, mainly due to a similar increment of the FC contribution, and that all intermolecular couplings decay drastically beyond couplings between next neighbor units while again the FC term is the main contribution for closest neighbor couplings, one can conclude that due to the formation of the hydrogen bonds the electron density in each unit is modified in a way that favors the intramolecular electronic transmission of the spin−spin coupling, in particular the FC mechanism, but also to a minor extent the PSO mechanism.

4. Concluding Remarks

In this work we report a theoretical study of the inter- and intramolecular indirect nuclear spin−spin coupling constants in the series of complexes $(HCN)_n$ and $(HNC)_n$ ($n = 1-6$) as well as of the interaction energies of the monomers in the complexes. The optimization of the geometries and the calculation of the interaction energies were performed at the MP2/cc-pVTZ frozen core level of approximation, whereas the indirect nuclear spin−spin coupling constants were calculated with the SOPPA approach and locally dense basis sets based on the cc-pVTZ-J basis sets.

We can confirm the previously observed cooperativity effects for the interaction energies in both series of chains. All intermolecular distances also exhibit a cooperative effect. Furthermore, the interaction energies as well as the intermolecular distances in the two series correlate very well with each other.

The main goal of this study, however, is the analysis of the intra- and intermolecular indirect spin−spin coupling constants and their four Ramsey contributions.

The intermolecular as well as intramolecular couplings in the $(HCN)_n$ series correlated very well with the corresponding couplings in the $(HNC)_n$ series.

The Fermi contact term is the largest contribution to both intra- and intermolecular couplings with the exception of two intramolecular couplings in the monomers where the PSO and SD terms are larger.

In both monomers, HCN and HNC, the ^1J(N,C) coupling has a very important SD contribution with the same sign as the FC term. In HNC, the SD term is actually larger than the FC term, whereas it amounts to about 60% of the FC term in HCN. Furthermore, the two-bond coupling constants exhibit very large PSO contributions which have the same sign as FC. For HCN, the PSO term is almost as large as the FC contribution. In HNC it amounts to about 40% of the FC term.

Remarkable is the fact that the FC term is the only important contribution to the intermolecular coupling constants and that its value, expressed as reduced coupling constant, K, is negative for coupled nuclei which are the acceptor and hydrogen in the hydrogen bond. This may confirm the noncovalent nature of the interaction between these two atoms as pointed out by Arnold and Oldfield. However, in HB complexes between charged molecules, where the interaction is stronger, the sign of the coupling constant changes.[44]

The effect of the other units in an oligomer on the one-bond NC coupling and the two-bond NH and CH couplings in one unit of a complex is mainly an increase in the FC contribution and thus in the total indirect coupling. The couplings thus exhibit a cooperativity effect in the same sense as the HB distances. The predominance of the FC contribution as well as the small changes observed for the SD and the PSO terms may be due to the fact that there is no significant overlap between the π-orbitals of the units from which the complexes are built. Consequently, there is not a strong mesomeric effect in these types of complexes. However, the increment of the reduced couplings $^{2h}K(C_{(i+1)},N_{(i)})$ in $(HNC)_n$ compared to $^{2h}K(N_{(i+1)},C_{(i)})$ in $(HCN)_n$ may at least partially be due to an electromeric effect, i.e., electron transfer.

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Supporting Information Available: A complete list of the four intra- and intermolecular contributions to the indirect spin−spin coupling constants for $(HCN)_n$ and $(HNC)_n$ complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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