Theor Chem Acc (1998) 99:116–123

Theoretical
Chemistry Accounts

Regular article

Isocyanides as hydrogen bond acceptors

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Received: 13 October 1997 / Accepted: 11 December 1997

Abstract. A theoretical study of the capability of hydrogen isocyanide (HNC) as a hydrogen bond acceptor has been carried out. The geometry, interaction energy and electronic properties of the corresponding complexes with HF, HCl, HBr, H_2O, NH_3, HCCH, HCN and HNC itself indicate that it is able to form strong hydrogen bonds. A search in the Cambridge Structural Database has shown the presence of isocyanides involved in hydrogen bonds in solid phase. Finally, the comparison of the properties of HNC with its isomer, hydrogen cyanide, shows strong similarities between both compounds.

Key words: Hydrogen bonds – Isocyanides – Atoms in molecules methodology

1 Introduction

The continuous theoretical and experimental search for new groups involved in hydrogen bonds (HBs) has dealt with the appearance of non-standard hydrogen acceptors as π-systems [1], carbenes, silylenes [2], carbocations [3] and hydrogen (in dihydrogen bonds) [4, 5] and hydrogen donors as C-H groups [6].

One of the most interesting cases for the organic chemist corresponds to that in which two carbon atoms are involved in the HB. This case was simultaneously described for the first time by Ferstanding [7] and Schleyer and Allerhand [8] in 1962. The IR spectroscopy experiments showed that the carbon atom of the isocyanide moiety, acting as hydrogen acceptor (RNC···HX), was able to form strong HBs with standard hydrogen donors and other compounds like acetylenes.

The isocyanides and isonitriles are highly reactive species which were discovered in 1867 [9]. However, general methods for their preparation were not available until 1960 [10]. The appearance of naturally occurring isocyanides [11] has increased interest in this unique organic functional group.

Previous theoretical studies have addressed the ability of these compounds to act as hydrogen bond acceptors. Thus, Kollman et al. [12] calculated the interaction energy of a series of proton donors with hydrogen isocyanide at the HF/4-31G level of theory. Tang and Fu [13] studied the complexes of methylisocyanide and methylcyanide with methanol at the same level of theory.

In this article, the properties (geometry, interaction energy, charge redistribution, electron density topology and NMR shifts) of the HB formed by HNC with eight hydrogen donors are studied theoretically. In addition, a search in the Cambridge Structural Database (CSD) [14] is performed to identify some cases of this kind of HBs in solid phase. Finally, a comparative study of HNC and hydrogen cyanide (NCN) is carried out.

2 Methods

HB complexes of HCN with seven well-known hydrogen donors and with a complex HNC itself have been studied. For the eight complexes studied, a linear or almost linear disposition of the C···HX moiety has been considered, where C corresponds to the carbon atom of HNC and HX corresponds to the hydrogen donor molecule where X = F, Cl, Br, OH, NH_2, CN, NC or CCH. Symmetry conditions have been imposed when possible.

The geometries of the monomers and the complexes have been fully optimized with the Gaussian-94 program [15] using the standard 6-31G** [16] and 6-311++G** [17] basis sets at the Hartree-Fock (HF) and second order Møller-Plesset (MP2) [18] perturbation theory levels, respectively. In addition, a hybrid restricted Hartree-Fock (RHF)-density functional method (Becke3LYP) [19] has been used with the largest basis set.

In all the calculations, the minimum nature of the monomers and complexes has been confirmed by calculating the corresponding frequencies. The interaction energies, $E_I(AB)$, have been calculated as the difference between the energy of the complex and the sum of the energies of the monomers (Eq. 1):

$$E_I\,(AB) = E(AB)_{AB} - [E(A)_A + E(B)_B] \quad (1)$$

where $E(AB)_{AB}$ represents the energy of the complex and $E(A)_A$ the energy of the isolated monomer A calculated with its corresponding basis set.

In addition, a corrected interaction energy, E_{CORR} of the inherent basis set superposition error (BSSE), and zero-point energy

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Correspondence to: I. Alkorta (e-mail: ibon@pinarl.csic.es) correction (E_{ZPC}) has been evaluated. The BSSE has been calculated using the Boys-Bernardi counterpoise technique [20] and Eq. (2):

$$E_{BSSE}(AB) = E(A')_A - E(A')_{AB} + E(B')_B - E(B')_{AB} \quad (2)$$

where $E(A')_{AB}$ represents the energy calculated for monomer A using its geometry in the complex and the complete set of basis functions used to described the dimer, and $E(A')_A$ the energy of the structure of monomer A on the complex calculated with its corresponding basis set.

E_{ZPC} has been carried out using Eq. (3):

$$E_{ZPC}(AB) = E(AB)_{ZP} - [E(A)_{ZP} + E(B)_{ZP}]. \quad (3)$$

Finally, the corrected interaction energies have been calculated with Eq. (4):

$$E_{CORR}(AB) = E_I(AB) + E_{BSSE}(AB) + E_{ZPC}(AB). \quad (4)$$

The topological properties of the electronic charge density have been characterized using the atoms in molecules (AIM) methodology [21] with the AIMPAC program package [22]. A 0.001 e/a.u^3 electron density has been used to define the molecular radii in the hydrogen bond direction. The interpenetration of the electronic clouds in the formation of the HB has been calculated as the difference of the atomic radii in the HB direction of the isolated monomers, using the above-indicated electron density, and the position of the HB critical points in the complex.

The nuclear magnetic resonance (NMR) spectroscopic properties of the isolated molecules and complexes have been calculated using the GIAO perturbation method [23] as implemented in the Gaussian-94 program.

In order to be able to predict properties of complexes not studied, different relationships between the calculated properties have been examined. In addition, these relationships could reflect the influence of properties that were considered in principle to be non-related.

A search in the CSD has been carried out in order to find examples of isocyanides involved in HB in solid phase. All the crystal structures with the isocyanide moiety have been retrieved from the database using the CONNSER module, excluding those with metals, disorder and imposing the error-free less than 0.002 Å condition. The possible HBs in these crystal structures have been explored with the GSTAT module.

Finally, a comparison of the isomeric compounds, HNC and HCN molecules, has been carried out using their geometric and electronic properties, as previously described for the monomers and HB complexes. In addition, the molecular electrostatic potential in the molecular plane has been calculated for both molecules using the GRID option in the Gaussian-94 program.

3 Results and discussion

3.1 Hydrogen bonded systems

The geometrical parameters of the hydrogen-bonded systems studied here are collected in Table 1. As shown in other reports, the RHF/6-31G** results provide longer HB distances than those obtained with methods that include electron correlation (B3LYP and MP2 in this case). If the MP2/6-311++G** values are used as a reference, those obtained at the RHF/6-31G** level are on average 13% longer and those at the B3LYP/6-311++G** level are 4% shorter. In addition, the comparison of these methods indicates that the HB distances obtained at the MP2/6-311++G** and B3LYP/6-311++G** levels follow a more similar trend ($r^2 = 0.985$) than any of these two methods compared with RHF/6-31G** (MP2/6-311++G** vs RHF/6-31G**: $r^2 = 0.972$ and B3LYP/6-311++G** vs RHF/6-31G**: $r^2 = 0.943$).

A more detailed analysis of the results indicates that HB distances, in the studied complexes, increase from the shortest (1.95 Å, for HF) to the longest (2.63 Å, for H_3N and HCCN) in regular steps (2.09 Å for HNC, 2.20 Å for HCl, 2.27 Å for H_2O and HBr, and 2.41 Å for HCN). This distribution will provide a good basis to compare the possible relationship of different properties of these complexes with the HB distance.

No experimental gas phase data are available for HB complexes of HNC. For this reason, it was considered interesting to compare the present results with the available experimental data for hydrogen cyanide acting as an HB acceptor. The observed HB distances for the HCN···HX systems (HX = HF, HCl, HBr and HCN) [24] are about 0.08 Å shorter than the ones calculated here for the corresponding HNC···HX at the MP2/6-311++G** level. In principle, this fact could be an indication of the weakness of these hydrogen bonds; however, the electron donor atom is different in both cases and in fact the atomic radius of the carbon atom (1.75 Å) is much larger than that of nitrogen (1.55 Å) [25]. In addition, the bond elongation of HF in the formation of HB is almost the same in the experimental data for HCN···HF and in the calculated data for HNC···HF (0.014 Å).

The geometrical effects of the formation of the HB on HNC are a shortening of the CN bond (by as much as 0.006 Å in the HNC···HF complex) and a small lengthening of the N-H bond (0.001 Å in the same complex). These facts can be explained based on the geometry of the protonated $HNCH^+$ cation, the final product of the proton transfer, that presents a shorter CN bond (0.033 Å shorter than in HNC) and a longer HN bond (0.017 Å longer than in HNC). These effects, especially the CN shortening, are more important for

Table 1. Distance (C···H, Å) and angle (C···HX, °) of the hydrogen bonds

	RHF/6-31G**		B3LYP/6-311++G**		MP2/6-311++G**	
	Dist.	Ang.	Dist.	Ang.	Dist.	Ang.
HNC···H_2O	2.3916	172.59	2.2287	178.46	2.2671	177.30
HNC···HCN	2.4419	180.00	2.3751	180.00	2.4069	180.00
HNC···HF	2.0822	180.00	1.8979	180.00	1.9532	180.00
HNC···HNC	2.2148	180.00	2.0890	180.00	2.0901	180.00
HNC··· H_3N	2.6807	173.38	2.5557	176.45	2.5858	176.88
HNC···HCl	2.3031	180.00	2.1127	180.00	2.1967	180.00
HNC···HBr	2.4330	180.00	2.1922	180.00	2.2721	180.00
HNC···HCCH	2.6269	180.00	2.5677	180.00	2.5781	180.00

complexes with smaller HB distances. Thus, a linear tendency is observed between these two distances with an $r^2 = 0.92$.

The interaction energy, BSSE, ZPC and the corrected interaction energies of the complexes studied are shown in Table 2. The comparison of the three methods used here shows similar interaction energies and ZPCs for all the methods. However, regarding the BSSE, the larger correction corresponds to the RHF/6-31G** method followed by MP2/6-311++G** and finally, B3LYP/6-311++G**, which that shows very small BSSE corrections. A quantitative analysis of the correction energies (ZPC and BSSE) indicates that the ZPC value ranges from 44% of the corresponding interaction energy in the HNC···H_3N complex to 19% in the HNC···HBr complex. The same comparison in the case of BSSE indicates that the larger relative correction corresponds to the HNC···HCl complex (18%) and the smallest to HNC···HNC (8%). The present analysis indicates the importance of including the ZPC for a correct description of the interaction energy, it is more important than the inherent BSSE, especially when large basis sets are considered.

The final corrected energies obtained indicate that the RHF/6-31G** method underestimates this value when compared to the other two methods that provide similar results.

The energy values for the different complexes ranged from a very weak interaction in the HNC···H_3N complex (E_{CORR} less than 1 kcal/mol), as can be expected from the long HB distance observed, to a strong HB (E_I more than 7 kcal/mol, and E_{CORR} over 5 kcal/mol) in the case of the HNC···HF and HNC···HNC complexes. This value is similar to the experimental interaction energy of the water dimer ($E_I = -5.2$) [26].

All attempts to find any correlation between HB distance and the interaction energies and energy corrections have been unsuccessful.

Another measure of HB strength corresponds to the electron transfer, which is calculated using the AIM charges, and the electron density at the HB critical points (CP) (Table 3). The large electron transfer and electron density values at the CP for most of the complexes studied, except HNC···H_3N and HNC···HCCH, confirm the strength of these HBs (for comparative purposes: the electron transfer, CP electron density and interaction energy values of the H_2O···HF complex reported in the literature [27] are 0.023 e, 0.0276 e and 8.32 kcal/mol, respectively). The positive value of the Laplacian shows that they are closed-shell interactions. Analysis of the electron flow indicates that the hydrogen and nitrogen atoms of HNC act as an electron reservoir. Thus, the nitrogen atom loses twice as many electrons as the hydrogen in favour of the carbon atom; this slightly decreases the net positive charge of the carbon atom and the electron acceptor molecule. This electron movement is reflected in the typical dipole moment enhancement (DME) observed in HBs. As expected, stronger HBs show larger DME; however, a more detailed analysis indicates the importance of the electronegativity and

Table 2. Interaction energy (E_I), basis set superposition error (BSSE) (E_{BSSE}) and zero-point energy correction (ZPC) (E_{ZPC}) and corrected interaction energy (E_{CORR}) (kcal/mol) of the complexes studied

	RHF/6-31G**				B3LYP/6-311++G**				MP2/6-311++G**			
	E_I	E_{BSSE}	E_{ZPC}	E_{CORR}	E_I	E_{BSSE}	E_{ZPC}	E_{CORR}	E_I	E_{BSSE}	E_{ZPC}	E_{CORR}
HNC···H_2O	−3.769	0.92	1.38	−1.47	−3.832	0.17	1.39	−2.27	−4.141	0.49	1.41	−2.24
HNC···HCN	−4.771	0.88	1.18	−2.71	−4.149	0.12	1.00	−3.03	−4.716	0.42	1.03	−3.27
HNC···HF	−6.933	1.17	1.82	−3.94	−8.238	0.32	2.04	−5.88	−7.821	0.72	2.08	−5.02
HNC···HNC	−6.406	1.08	1.57	−3.76	−6.583	0.17	1.42	−4.99	−7.516	0.62	1.50	−5.40
HNC··· H_3N	−1.858	0.71	0.93	−0.22	−1.536	0.11	0.91	−1.05	−2.065	0.38	0.9	−0.79
HNC···HCl	−4.553	1.11	1.55	−1.89	−4.967	0.43	1.54	−3.00	−5.165	0.93	1.35	−2.89
HNC···HBr	−3.514	0.79	1.22	−1.50	−3.832	0.20	1.31	−2.32	−4.294	0.65	0.82	−2.82
HNC···HCCH	−2.415	0.76	0.93	−0.73	−1.943	0.13	0.80	−1.01	−2.551	0.38	0.78	−1.39

Table 3. Electron transfer (e), atomic charges (e), dipole moment enhancement, (DME) (debye) and electron density properties at the HB critical point using the atoms in molecules (AIM) methodology at the MP2/6-311++G** level

	Electron transfer	ΔC^a	ΔN^b	ΔH^c	DME	ρ (e/a.u.^{3})	∇^2 (ρ) (e/a.u.^{5})
HNC···H_2O	−0.021	−0.0046	0.0154	0.0096	0.60	0.0149	0.0472
HNC···HCN	−0.017	−0.0127	0.0177	0.0115	0.75	0.0118	0.0361
HNC···HF	−0.048	0.0033	0.0272	0.0171	0.97	0.0285	0.0781
HNC···HNC	−0.035	−0.0095	0.0275	0.0172	1.19	0.0219	0.0610
HNC··· H_3N	−0.010	−0.0032	0.0070	0.0048	0.39	0.0084	0.0250
HNC···HCl	−0.027	−0.0051	0.0203	0.0121	0.90	0.0185	0.0513
HNC···HBr	−0.023	−0.0056	0.0179	0.0108	0.94	0.0163	0.0442
HNC···HCCH	−0.010	−0.0043	0.0087	0.0059	0.54	0.0084	0.0252

[a] Charge in isolated HNC: 0.9089

[b] Charge in isolated HNC: −1.4320

[c] Charge in isolated HNC: 0.5239

polarizability of the atoms present on these complexes in the effects observed in this property.

A good linear correlation has been found (Eq. 5) between the electron transfer and the electron density at the HB CP of the complexes at the MP2/6-311++G** level:

$$\rho(\text{HB CP, e/a.u.}^3) = 0.00361\text{–}0.52834\ (\text{electron transfer, e}),\ n = 8,\ r^2 = 0.995 \tag{5}$$

An attempt to obtain linear correlations between the electron transfer and the electron density at the HB CP with the HB distance gave the following results: $r^2 = 0.948$ and 0.964, respectively. However, as we have recently shown [28] a logarithmic relationship between the electron density at the HB CP and the HB distance can be found (Eq. 6):

$$\ln[\rho(\text{HB CP, e/a.u.}^3)] = 0.27694\text{–}1.95675\ (\text{HB distance, Å}),\ n = 8,\ r^2 = 0.995 \tag{6}$$

This correlation is able to explain very weak interactions, since long HB distances imply electron densities close to zero, and at small distances resemble the electron densities of covalent bonds. Thus, a unified relationship is able to correlate the values of these properties independently of the range studied, covalent bonds or HBs, which indicates that a similar rule can be applied to these two, in principle, different situations.

The properties of the hydrogen atom involved in the HB, calculated within the AIM methodology, have been used to characterize the interactions in a HB [29]. Some of these properties are collected in Table 4. As a general rule, the charge of the atom becomes more positive, and its energy and volume decreases. The charge variation observed seems to depend on the polarizability of the proton donor group. Thus, the smallest value corresponds to the complex with FH (0.0041 e) and the largest to the ones with HCl (0.0631 e) and HBr (0.0731 e). A similar tendency is observed with respect to the energetic destabilization of this atom. Regarding the atomic volume, an exception to the decrease of the hydrogen atom volume is observed in the case of the HNC···H_3N. As pointed out by Koch and Popelier [29], who found an exception to this rule, this feature cannot be considered as a necessary condition in the HBs. The fact that long distances are observed in the exceptional cases could indicate that this property does not follow asymptotic behaviour while the HB enlarges.

Another property associated with electron density is the interpenetration of the electronic clouds of the two monomers in the formation of the HB (Table 5). A surface contour value of 0.001 e/a.u.^{3} has been used for reference, since it has been found that this surface encloses a volume similar to the experimental molecular volume of the molecules. In all cases, the carbon atom electron cloud is penetrated more than that of hydrogen, probably due to the polarization effect produced in the formation of the HB that moves the electron cloud of HNC towards the electron acceptor monomer. The sum of the interpenetration of both fragments indicates an important flexibility of electron clouds, especially in the weakest cases (0.75 Å in the complexes with HCCH and H_3N). The upper limit of this value is defined by the

Table 4. Atomic properties (a.u.) of the hydrogen involved in the HB in the isolated monomers and in the HB complexes calculated using the AIM methodology at the MP2/6-311++G** level

	Charge		E(atom)		Volume	
	Isolated HB donor	Δ HB complex	Isolated HB donor	Δ HB complex	Isolated HB donor	Δ HB complex
HNC···H_2O	0.5666	0.0269	−0.3791	0.0188	17.3948	−1.0019
HNC···HCN	0.2046	0.0483	−0.5269	0.0241	29.9968	−1.0475
HNC···HF	0.7116	0.0041	−0.2957	0.0130	11.5688	−1.3808
HNC···HNC	0.5239	0.0326	−0.3906	0.0279	18.4759	−1.7601
HNC··· H_3N	0.3481	0.0293	−0.4852	0.0142	25.3588	0.0814
HNC···HCl	0.2518	0.0631	−0.5022	0.0331	29.2569	−2.7771
HNC···HBr	0.0579	0.0731	−0.5628	0.0353	36.9536	−2.9144
HNC···HCCH	0.1561	0.0406	−0.5497	0.0197	31.7999	−0.2294

Table 5. Interpenetration of the electronic clouds in the formation of the HB (Å) using as reference value the 0.001 e/a.u.^{3} isodensity surface (MP2/6-311++G**); CP, critical point

	r_H isolated HB donor	Distance from the C atom to the HB CP	Distance from the H atom to the HB CP	Δ r_C	Δ r_H	Δ r_H/Δ r_C	Δ r_C + Δ r_H
HNC···H_2O	1.2171	1.4789	0.7888	0.5743	0.4283	0.7458	1.0026
HNC···HCN	1.2436	1.5471	0.8599	0.5061	0.3837	0.7582	0.8898
HNC···HF	1.1271	1.3245	0.6287	0.7287	0.4985	0.6841	1.2271
HNC···HNC	1.1695	1.3913	0.6988	0.6619	0.4707	0.7111	1.1325
HNC··· H_3N	1.2753	1.6299	0.9564	0.4233	0.3189	0.7534	0.7422
HNC···HCl	1.2912	1.4316	0.7651	0.6216	0.5261	0.8464	1.1477
HNC···HBr	1.3229	1.4664	0.8057	0.5868	0.5173	0.8816	1.1040
HNC···HCCH	1.2700	1.6326	0.9456	0.4207	0.3244	0.7711	0.7451

nuclei-nuclei repulsion of the interacting atoms that is rapidly reached based on the values of Table 5 (1.23 Å for the HNC···HF complex).

The relationship $\Delta r_C/\Delta r_H$ provides a measure of the hardness of the different hydrogen atoms. Thus, the hardest one corresponds to HF and the weakest is that of HBr. A linear correlation between the total interpenetration, $\Delta r_C + \Delta r_H$, of the electronic clouds and the HB distance can be found ($r^2 = 0.972$). However, this relationship only makes sense in the range studied, since complexes with very long interaction distances should tend toward zero interpenetration and very short distance interactions would be limited by the nuclear repulsion as indicated before.

The effects of HB formation on spectroscopic signals have been known for a long time. A red shift of the stretch X-H signal is observed in IR spectroscopy and a displacement of the hydrogen signal of the atom involved in the HB is registered at lower fields in ^{1}H-NMR.

The harmonic frequencies of the X-H stretch of isolated and HB complexes (Table 6) show the expected red shift in all the complexes. The magnitude of these shifts is determined by two factors: (1) the strength of the HB interaction and (2) the strength of the X-H bond. In the calculated data, the first factor seems to be more important; thus, the largest shifts correspond to HNC···HF ($\Delta\nu = 332\ \mathrm{cm}^{-1}$) and HNC···HNC ($\Delta\nu = 280\ \mathrm{cm}^{-1}$) complexes and the smallest to the HNC···H_3N ($\Delta\nu = 20$ and $11\ \mathrm{cm}^{-1}$) system. The second effect can be observed in complexes such as HNC···HCl ($\Delta\nu = 166\ \mathrm{cm}^{-1}$) and HNC···HBr ($\Delta\nu = 131\ \mathrm{cm}^{-1}$) which show similar interaction energies. The present results are similar to those of Ferstanding [7] and Schleyer and Allerhand [8] who found a red shift of $250\ \mathrm{cm}^{-1}$ in the stronger complexes and $30\ \mathrm{cm}^{-1}$ in the case of a benzyl isocyanide-phenylacetylene complex. (Our model for this system, HNC···HCCH, indicates a $\Delta\nu$ of $34\ \mathrm{cm}^{-1}$ for the more intense harmonic frequency.)

Table 6. Harmonic frequencies of the X-H stretching (cm^{-1}) in the isolated HB donor and HB complexes calculated at the MP2/6-311++G** level

	Isolated HB donors	HB complexes
	4003	3974
H_2O	3884	3824, 3834
HCN	3483	3391
FH	4197	3865
HNC	3837	3557
	3683	3663
NH_3	3531	3520
ClH	3087	2921
BrH	2739	2608
	3550	3531
HCCH	3460	3426

The effects of the presence of these HBs in NMR spectroscopy have been predicted using the perturbation GIAO theory (Table 7). The chemical shieldings of the hydrogens that form the HB are moved to lower fields and those of the carbon atoms of HNC to higher fields. The relative variation of the ^{1}H-NMR signal of the proton involved in the HB is more important for complexes with HCl and HBr ($\Delta\sigma = -3.08$ and -3.02 ppm, respectively) than the rest of the complexes. In principle, the strongest HB complexes should show the biggest differences. However, this is only true if the same atoms are involved in the HB but, in this case, the nature of the atom attached to the hydrogen seems to be the determinant. As confirmation of this hypothesis, the variation of the ^{13}C-NMR of the HNC carbon atom, which should be less influenced by the nature of the X atoms, shows a good linear correlation with the HB distances calculated at the B3LYP/6-311++G** level ($r^2 = 0.966$).

A search in the CSD has shown that even though examples of this kind of HB can be found in solid state, they are very limited (only five using a cut-off distance of 2.5 Å for the C···H distance), as shown in Table 8. Four of the interactions found correspond to alcohols and only one, the largest, to an amine. Even though the present survey is not statistically significant, it is noteworthy that HBs formed with amines are very long, both theoretically and for those found in the CSD search.

3.2 Comparison between HNC and HCN

The analysis of the calculated and experimental parameters available for HCN and HNC (dipole moment, NMR shieldings and bond distances) indicates that the theoretical methods used here adequately reproduce the experimental data (Table 9).

Table 7. Calculated NMR shieldings (ppm) of the monomers and complexes using the GIAO perturbation theory at the B3LYP/6-311++G** level

	σ ^{1}H-NMR[a] (isolated molecules)	σ ^{1}H-NMR (HB complexes)	$\Delta\sigma$ ^{1}H-NMR	^{13}C-NMR of the HNC molecule	$\Delta\sigma$ ^{13}C-NMR[b]
H_2O	31.62	30.27	−1.35	15.59	7.16
HCN	29.57	28.35	−1.22	15.66	7.24
HF	30.24	27.45	−2.79	21.89	13.46
HNC	28.25	26.41	−1.84	19.31	10.88
H_3N	32.00	31.24	−0.76	11.69	3.27
HCl	31.29	28.21	−3.08	18.71	10.28
HBr	31.45	28.43	−3.02	17.55	9.12
HCCH	30.77	30.04	−0.73	12.17	3.74

[a] The indicated value corresponds to the hydrogens involved in the HB

[b] Referred to that of isolated HNC (see Table 10)

The energetic results for these two molecules indicate that the HCN tautomer appears to be 11.5 (RHF/6-31G**), 14.8 (B3LYP/6-311G**) and 18.7 kcal/mol (MP2/6-311++G**) more stable than HNC, which is similar to the approximately 15 kcal/mol difference in stability reported by others [30].

A comparison of different geometric and physicochemical characteristics shows that their molecule parameters have striking similarities. For example, their bond distances are very similar, which makes the total atomic distance between the molecular extremes almost identical. Even more impressive is the similarity in their molecular electrostatic potential (MEP) and in the value of the dipole moment (a complete picture of the MEPs of both molecules in their molecular plane is represented in Fig. 1). The position and value of the MEP minima are very similar in both cases, indicating that both molecules should form HBs with similar strength, or slightly stronger in the case of HNC, since its minimum is lower (−44.52 vs −41.96 kcal/mol). Another parameter that has been used to characterize the nucleophilic regions is the local minima in the $\nabla^2(\rho)$ surfaces [31]. The position of the corresponding minimum from the heavy atom extreme of the molecules shows only a difference of 0.07 Å although the value of the Laplacians is somewhat different (Fig. 2).

Table 8. Isocyanides involved in HB in the Cambridge Structural Database: A C···H distance cut-off of 2.5 Å has been used $-N{\equiv}C\cdots HX$

Ref. code	C···H (Å)	C···H-X (°)	NC···H (°)	Nature of X
BAVHUB	2.01	152.9	157.8	O
BAVHUB	2.06	176.3	168.0	O
HEXZIT	2.24	153.4	152.8	O
JIFFIN	2.30	139.2	158.2	O
LEGROE	2.44	165.5	173.2	N

One parameter that is dissimilar is the molecular radius of the heavy atom in the axial direction, $r_{0.001}$, defined by the 0.001 e/a.u^3 electron density isosurface. It shows that the carbon atom in HNC is 0.15 Å bigger than the nitrogen in HCN, which is close to the difference of the Gavezzotti's atomic radius (0.2 Å) [25]. This result, together with the fact that the length of the HB formed by these two compounds only differs by 0.08 Å, as mentioned above, indicates that HBs formed by HNC should be slightly stronger than those of HCN.

The parameters that are clearly different for these two molecules are the bond order of the multiple bond (calculated using the AIM methodology), and the calculated NMR shieldings. The bond order of the multiple bond is smaller in the case of the HNC. This result is in agreement with the proposed non-zwitterionic distribution with a double bond between the nitrogen and carbon in the case of the HNC, while in the case of HCN a triple bond is indicated. The NMR shifts, especially those corresponding to the carbon and nitrogen in the two compounds, confirm this different electronic distribution.

While this paper was in the editing process an article [32] was published in which ionic HBs in isocyanides were studied experimentally and theoretically in gas phase. The experimental results indicate that the interaction enthalpy of methylisocyanide with protonated amines is about 24 kcal/mol, similar to the HB formed between protonated amines and amines. Both, experi-

Table 9. Comparison of HNC and HCN (the uniform H-X-Y nomenclature has been used in this table). All the calculated values correspond to the MP2/6-311++G** level except the NMR shieldings (B3LYP/6-311++G**). MEP, molecular electronic potential

	Calculated dipole moment (debye)	Experimental dipole moment[a] (debye)	Distance from the MEP minima to Y (Å)	MEP minima value (kcal/mol)	Distance from ∇^2(r) minimum to Y(Å)	∇^2(r) minimum value (e/a.u.^{5})
HNC	3.31	3.05 ± 5%	1.47	−44.52	0.460	−1.173
HCN	3.00	2.98 ± 1%	1.39	−41.96	0.391	−2.568

	Molecular radius in the axial direction $r_{0.001}$ (Å)	Calculated X-H bond distance (Å)	Experimental X-H bond distance (Å)	Calculated C-N bond distance (Å)	Experimental C-N bond distance (Å)	Calculated bond order of the C-N bond.	Electron density at the CN CP. (e/a.u.^{3})
HNC	2.05	1.001	0.996[b]	1.181	1.168 [b]	1.883	0.410
HCN	1.90	1.068	1.065[c]	1.171	1.153[c]	2.383	0.455

	Absolute ^{1}H-NMR shielding (ppm)	Absolute ^{13}C-NMR shielding[d] (ppm)	Absolute ^{15}N-NMR shielding[e] (ppm)
HNC	28.25	8.43	94.21
HCN	29.57	74.65	−38.14

[a] Taken from Ref. [33]

[b] Taken from Ref. [34]

[c] Taken from Ref. [35]

[d] Experimental ^{13}C-NMR absolute shielding of HCN: 82.1 Ref. [36]

[e] Experimental ^{15}N-NMR absolute shielding of HCN: −20.4 Ref. [37]

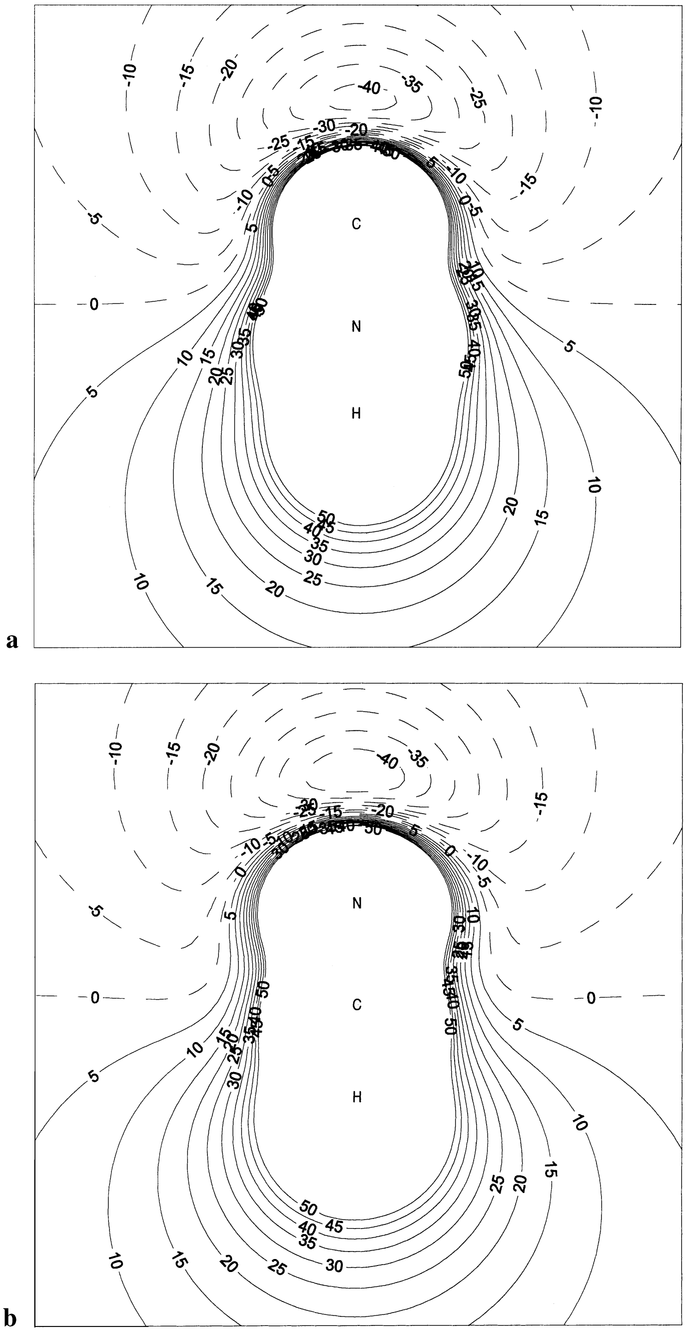

Fig. 1. MEP of **a** hydrogen isocyanide (HNC) and **b** hydrogen cyanide (HCN) in kcal/mol

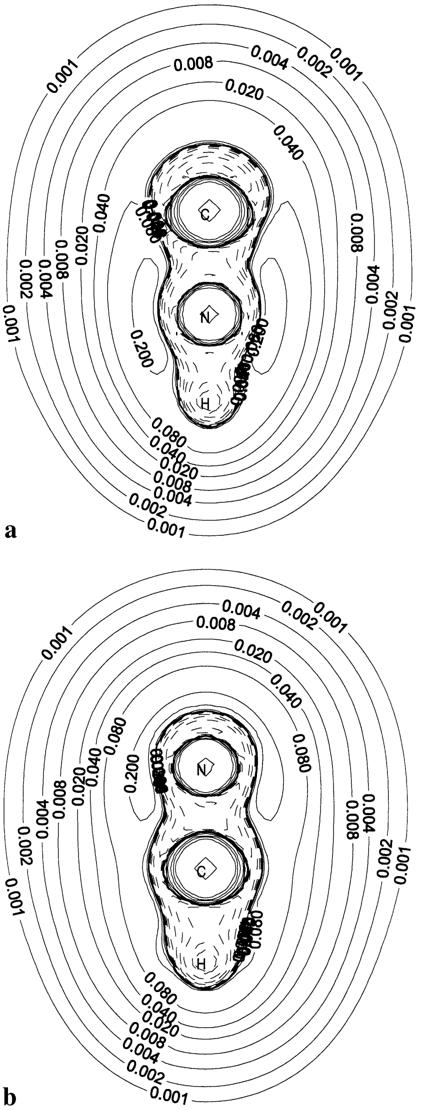

Fig. 2. $\nabla^2(\rho)$ plots of **a** HNC and **b** HCN in e/a.u.[5] *Dashed lines* correspond to negative values of this property

mental and calculated results indicate that isocyanides and cyanides complexes are nearly equal in stability.

4 Conclusion

In the present work the ability of isocyanides as HB acceptors has been studied. The ab initio calculations performed using HNC as an HB acceptor and eight proton donors have shown that the corresponding complexes could be as strong as the one formed in the water dimer [E_I (exp.) = −5.3, E_{CORR} (MP2/6-311++G**) = −2.1 kcal/mol]. Other parameters calculated at the MP2/6–311++G** level of theory, such as the electron density at the bond CP, electron transfer, atomic properties of the hydrogen involved in the HB and perturbation of the IR and NMR signals, confirm this conclusion.

A comparison of HNC with its isomer HCN shows strong similarities between the two molecules. A striking fact is that the carbon atom in isocyanides act in a similar way to the nitrogen atom in cyanides, generating a deep MEP minima near the carbon atom which results in strong HBs in these compounds.

A search in the CSD has shown the presence of this interaction in solid phase. Finally, a comparison of HNC and its isomer, HCN, a standard HB acceptor, shows their similarity, especially regarding their electronic and geometric properties, indicating that isocyanides could be as good HB acceptors as cyanides.

Acknowledgements. Thanks are given to the EU for the network Location and Transfer of Hydrogen (No. CHRX CT 940582) and the Spanish project SAF97-0044-C02.

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