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A Theoretical Study of the HCN ⇋ HNC Isomerization and of the Cyano- and Isocyanoborohydride Ions

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The ab initio *LCAO–MO–SCF calculation has been used to investigate the HCN⇋HNC isomerization. It is shown that either intramolecular or intermolecular mechanisms are possible, although a different probability of realization can be expressed. The geometrical and electronic structures of both the cyano- and isocyano-borohydride ions BH_3CN^- and BH_3NC^- are calculated and the charge transfers and bond formation discussed, in particular* versus *the direct $BH_3 + CN^- \rightarrow BH_3CN^-$ synthesis.*

The non-equivalent reducing behaviour of the borohydride ion BH_4^- and of the cyanoborohydride ion BH_3CN^- is rationalized in terms of the electronic charge distribution in these molecules.

Introduction

During the last years, the general importance of the boron–cyano compounds has become increasingly evident and the existence of some related isocyano compounds has been clearly established on the basis of chemical behaviour and spectroscopic analysis. However very scant information is reported in the literature either about the mechanisms of formation of these species or about their isomerization. In particular, the direct synthesis of the isocyanoborohydride ion BH_3NC^- from HCN [1] (simultaneously with the normal BH_3CN^- ion) supposes the previous presence of the isohydrogen cyanide HNC in the reactional mixture. Therefore this work essentially deals with a theoretical study of the mechanism of the HCN⇋HNC isomerization; in the second part, the geometrical and electronic structures of both the iso- and normal cyanoborohydride ions are determined and discussed.

Theoretical Part

The non empirical *ab initio* SCF–MO calculations have been performed on the UNIVAC 1110 computer of the Nuclear Research Center of Strasbourg-Cronenbourg using an adapted Polyatom (version 2) program [9]. The MO basis set was generated from linear transformation of an AO basis; the latter in turn was obtained by the contraction from a set of primitive Gaussian type functions.

The HCN⇋HNC isomerization schemes were carried out using the triple zeta quality basis set of Dunning [2] and the geometry optimization and electronic structures of CN^-, BH_3, BH_4 and of the cyanoborohydride ions were calculated from the corresponding double zeta basis set. Details of the composition of the basis sets are summarized in Table I.

Results and Discussion

Intramolecular HCN⇋HNC Isomerization

The intramolecular isomerization of hydrogen cyanide to isohydrogen cyanide can be described by the migration of the proton from the carbon to the nitrogen atom of the same molecule. This displacement can be fully parametrized (Fig. 1-A) by the C–N bond length, the R_H distance of the proton to the middle of the C–N segment and the θ angle between NC and RH ($\theta = 0°$ for HCN and $\theta = 180°$ for CNH).

The optimization of the geometry is performed by varying simultaneously these parameters until the minimal total energy of the molecule is obtained. Variation steps are 0.01 Å for the distances and 0.5 degrees for the angles. Results are reported in Table II.

As was shown in earlier and more simple calculations [3] the transition state between the two isomers is not the classical T-shaped ($\theta = 90°$) molecule found by Van Dine and coll. [4], but an intermediate configuration with $\theta = 78°$. The corresponding electronic structures are reported in Table III.

We observe that the isomerization of HCN to the iso compound HNC is followed by the increase of the negative charge on the nitrogen (–0.64 e) whereas a positive charge appears on the carbon (+ 0.18 e). The charge of the hydrogen keeps positive but the atomic population of this atom is reinforced in HCN. The population is highest in the transition state where the carbon can be considered as neutral between the equally charged hydrogen ($\cong$ + 0.2e) and nitrogen ($\cong$ – 0.2 e) atoms.

TABLE I. Contracted Gaussian Basis Sets Used in Calculations.

Chemical System	Basis	Size	Basis	Type	Contraction Scheme [2]
	Prim.	Contr.	Prim.	Contr.	
B	24	10			
C	24	10	9s, 5p	[4s, 2p]	(1,2,3,4,5,6) (7) (8) (9)/(10,11,12,13) (14)
N	24	10			
H	4	2	4s	[2s]	(1,2,3) (4)
BH_3CN^- BH_3NC^-	84	36			
C	24	10	9s, 5p	[4s, 2p]	(1,2,3,4,5,6) (7) (8) (9)/(10,11,12,13) (14)
N	24	10			
CN^-	48	20			(1,2,3) (4)
B	24	10	9s, 5p	[4s, 2p]	(1,2,3,4,5,6) (7) (8) (9)/(10,11,12,13) (14)
H	4	2	4s	[2s]	(1,2,3) (4)
BH_3	36	16			
BH_4^-	40	18			

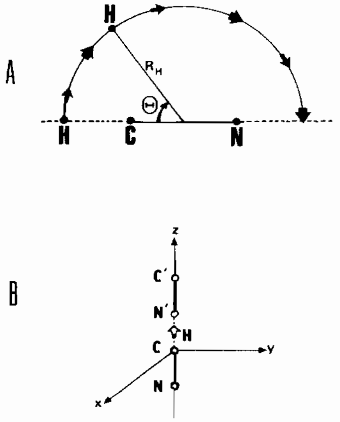

Figure 1. Geometrical parametrization of the intramolecular (A) and intermolecular (B) HCN⇋HNC isomerization.

In the HNC molecule, the increasing electronic population of the nitrogen is essentially localized in the p(E) orbitals (~0.95 e) whereas the 2s orbital loses 0.3 e. The inverse of this situation is observed on the carbon since the 2s orbital population increases appreciably (~0.65 e) and the p(E) orbitals lose 0.85 e.

The carbon–nitrogen overlap population of the isohydrogen cyanide HNC (~1.05 e) has mainly pi character (80%). This overlap is more important in HCN (1.85 e) but the pi character falls to 56%. In the latter, the main sigma contributions are generated by the ($2p_{z_N}^* \, 2s_C$) and ($2p_{z_N}^* \, 2p_{z_C}$) overlap. The C–H (in HCN) and N–H (in HNC overlap populations are sensibly of the same magnitude (0.6 e).

In a general way, the electronic transfers during the intramolecular HCN⇋HNC isomerization are considerable and the sigma/pi distribution of the carbon–nitrogen bond is appreciably perturbed. The HCN molecule is slightly more stable than the isocompound HNC (ΔE = 5.9 kcal/mol); however an important activation energy (64 kcal/mol) is necessary to follow the intramolecular HCN⇋HNC way and hard experimental conditions must be applied to realize it.

Intermolecular HCN⇋HNC Isomerization

As has been shown in earlier publication [1], the cyanide ion is involved in the cyano–isocyano com-

TABLE II. Geometrical Parameters and Energy Variations During the Intramolecular HCN⇋HNC Isomerization.

θ Angle (degrees)	Total energy (a.u.)	CN optimized (a.u.)	R_H Optimized (a.u.)
0° (HCN)	-92.84300	2.15	3.08
45°	-92.78471	2.18	2.73
70°	-92.74376	2.22	2.36
78°	-92.74125	2.23	2.23
80°	-92.74147	2.23	2.21
90°	-92.74613	2.24	2.13
110°	-92.76417	2.26	2.21
180° (HNC)	-92.83362	2.19	2.95

TABLE III. Electronic and Overlap Populations During the Intramolecular HCN⇋HNC Isomerization.

Atom	Orbitals	$\theta = 0°$ H–CN	$\theta = 45°$	$\theta = 70°$	$\theta = 78°$	$\theta = 80°$	$\theta = 90°$	$\theta = 110°$	$\theta = 180°$ H–NC
C	1 s	1.993	1.993	1.993	1.993	1.993	1.993	1.993	1.993
	2 s	1.161	1.384	1.730	1.808	1.821	1.865	1.871	1.835
	2 p_x	0.945	1.027	0.780	0.681	0.658	0.546	0.377	0.522
	2 p_y	0.945	0.815	0.677	0.660	0.661	0.671	0.700	0.522
	2 p_z	1.113	0.900	0.897	0.902	0.904	0.916	0.950	0.941
	Charge	−0.157	−0.119	−0.077	−0.044	−0.037	+0.009	+0.109	+0.187
N	1 s	1.994	1.993	1.993	1.993	1.993	1.993	1.993	1.993
	2 s	1.773	1.803	1.826	1.838	1.838	1.842	1.804	1.472
	2 p_x	1.055	0.838	0.710	0.723	0.735	0.807	1.011	1.478
	2 p_y	1.055	1.185	1.323	1.340	1.339	1.329	1.300	1.478
	2 p_z	1.303	1.341	1.326	1.306	1.304	1.286	1.277	1.222
	Charge	−0.180	−0.160	−0.178	−0.200	−0.209	−0.257	−0.385	−0.643
H	1 s	0.662	0.720	0.744	0.755	0.754	0.752	0.723	0.543
	Charge	+0.338	+0.280	+0.256	+0.245	+0.246	+0.248	+0.277	+0.457
C–N	Overlap	1.842	1.415	0.719	0.550	0.532	0.480	0.592	1.001
C–H		0.632	0.710	0.522	0.408	0.380	0.245	0.045	−0.004
N–H	Populat.	−0.021	−0.060	0.055	0.137	0.157	0.265	0.470	0.567

pounds isomerization, and an intermolecular mechanism including CN^- can be imagined between these species. This procedure is outlined (Fig. 1-B) by the displacement of the proton H of a molecule of hydrogen cyanide (noted NCH) toward a cyanide ion (noted $C'N'^-$) along the Oz axis as far as the new NC^- and HN′C′ moieties are theoretically formed. This operation is performed at various distances CN′ of the two molecules, with CN′ $\geqslant$ 2.03 Å, sum of the C–H–N′ covalent radii [5]. In every case, the total energy E_T of the system is calculated as a function of the CH length; the CN (1.14 Å) and C′N′ (1.16 Å) distances are optimized values. A series of results are plotted in Fig. 2. From the energetical point of view, the most stable systems are obtained when 5 a.u. $\leqslant$ CN′ $\leqslant$ 6 a.u. When this distance is greater than 7.0 a.u., the removal of the proton from the NCH molecule is complete, since the C–H overlap population rapidly becomes negligible ($\leqslant$0.1 e) and the H–N′ overlap increases up to the level observed for an individual HNC molecule.

The minimum of the total energy corresponds to the HCN and HNC molecules respectively in the presence of a cyanide ion and without appreciable interaction. The isomerization mechanism appears thus possible, as soon as the activation barrier is reached (~60 kcal/mol), and this situation is energetically quite equivalent to the one observed in the intramolecular process.

On the contrary, when HCN and the CN^- ion are very close one to the other, important interactions appear; in particular, the CH bond is not broken by the removal of the hydrogen towards the $N'C'^-$ ion, and the corresponding overlap population remains important (0.5 e). Moreover the H–N′ overlap is small and even becomes antibonding when C–N′ < 2.5 Å.

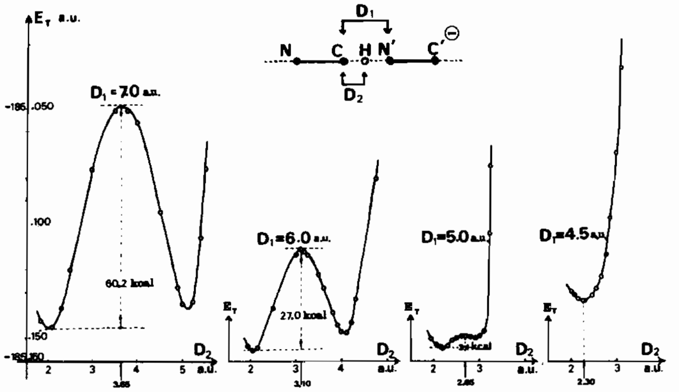

Figure 2. Energetical variations of the NC – H – $N'C'^-$ system during the proton intermolecular migration.

Thus under these particular conditions, we observe no longer the isomerization of the hydrogen cyanide, but the formation of an intermediate $(NC{-}H{-}N'C')^-$ complex ion, and the stability of the latter quickly decreases when the CN′ distance decreases, as a consequence of vigorous electronic repulsions.

In conclusion, both intramolecular and intermolecular mechanisms are theoretically possible, although the latter may be considerably perturbed by complex molecular association; however, even when the favorable conditions described above are realized, important thermal or photoactivation must be applied to generate HCN⇆HNC isomerization. Unfortunately the literature reports no experimental study on this subject probably as a consequence of the very bad stability of the HNC molecule; however, our results agree with experimental data on more elaborated cyano and isocyanocompounds, and in particular in the $(BH_3CN^-{-}BH_3NC^-)$ mixture [1], the total isomerization to BH_3CN^- can be observed after refluxing during several hours in the presence of HCN.

In the last part of this work, we have calculated the geometric and electronic structures of both BH_3CN^- and BH_3NC^- ions. The optimized geometry is determined by the simultaneous variation of all the parameters (BH, BC, CN, $\overleftarrow{CBH}$, for BH_3CN^- and BH, BN, NC, $\overleftarrow{NBH}$ for BH_3NC^-) until the minimal total energy is obtained. The step size applied for these variations is 0.01 Å for the distances and 0.5 degree for the angles and the C_{3v} symmetry is used to describe the molecules. The cyanoborohydride ion BH_3CN^- turns out to be energetically the most stable (ΔE = 7.9 kcal/mol) and the following parameters have been calculated: BC = 1.62 Å, BH = 1.23 and $\overleftarrow{CBH} = 108^\circ.5$. However, the geometry of the cyanoborohydride ion BH_3NC^- is very close to the latter and in particular the BH_3 group remains unaltered: BN = 1.58 Å, NC = 1.17 Å, BH = 1.23 Å and $\overleftarrow{NBH} = 108^\circ.5$.

The electronic populations and the main overlap population of both cyanoborohydride species are reported in Table IV. The charge of the BH_3CN^- ion is essentially localized on the boron (0.52 e) and the nitrogen (0.32 e) whereas the carbon and the hydrogen atoms can be considered as neutral. An important carbon–nitrogen overlap population (1.94 e) is observed. In the isocyanoborate BH_3NC^- on the contrary, the negative charge of the ion is delocalized on the whole molecule and the carbon now possesses an electronic excess over the boron (0.37 e) and nitrogen (0.22 e) atoms. On the hydrogens, the charge is virtually identical on both BH_3CN^- and BH_3NC^-, as previously observed with CH_3CN and CH_3NC [10]; however, in the latter series, these atoms are strongly positive (+0.33 e) in contrast with the nearly neutral situation observed in the boron compounds.

TABLE IV. Electronic Structures and Overlap Populations of the Free BH_3, CN^-, BH_4^- Species and of the Cyano and Isocyanoborohydrides Ions.

Atom	Orbital	Free BH_3	Free CN^-	BH_3CN^-	BH_3NC^-	BH_4^-	Balance sheet of $BH_3 + CN^- \rightarrow BH_3CN^-$ (– = loss, + = gain)	Balance sheet of $BH_3 + CN^- \rightarrow BH_3NC^-$
B	s	3.070		3.000	2.988	2.788	−0.070	−0.082
	$p(A_1)$	0.000		0.624	0.518	0.716	+0.624	+0.518
	p(E)	1.850		1.899	1.861	1.432	+0.049	+0.011
	Charge	+0.080		−0.522	−0.366	+0.064	Total + 0.603	Total + 0.447
H	s	1.027		1.027	1.051	1.267	0.000	+0.024
	Charge	−0.027		−0.027	−0.051	−0.267		
C	s		3.852	3.331	3.752		−0.521	−0.100
	$p(A_1)$		1.159	1.114	1.196		−0.045	+0.037
	p(E)		1.526	1.628	1.314		+0.102	−0.212
	Charge		−0.537	−0.073	−0.262		Total −0.464	−0.275
N	s		3.639	3.632	3.504		−0.007	−0.135
	$p(A_1)$		1.350	1.318	1.051		−0.032	−0.299
	p(E)		2.474	2.374	2.664		−0.100	+0.190
	Charge		−0.463	−0.324	−0.219		Total −0.139	Total −0.244
Overlap								
C–N			1.273	1.942	1.525			
B–C or B–N				0.486	0.354			
B–H		0.818	0.836	0.836	0.816	0.762		

In order to obtain more information on the B–N and B–C bonds in the cyano- and isocyanoborohydride ions, the electronic structures of the free CN^- and BH_3 molecules have been calculated (Table IV) and their geometries optimized (C–N = 2.20 a.u. and B–H = 2.24 a.u. according the earlier work [6]. The results are compared to the corresponding BH_3CN^- and BH_3NC^- electronic structures and the orbital population balance-sheet of the reaction $BH_3 + CN^- \rightarrow BH_3CN^-$ or BH_3NC^- is reported (Table IV).

In the cyanoborohydride ion, the formation of the B–C bond is accompanied by a transfer of 0.6 e to the p(E) orbital of the boron, essentially submitted by the s orbitals of the carbon. The other orbitals are weakly perturbed since the variations of their population are lower then 0.1 e. The B–C overlap population (0.49 e) has mainly sigma character.

In the isocyanoborohydride ion, the B–N bond is also formed with increasing boron $p(A_1)$ population (0.5 e). However, and in contrast with BH_3CN^-, the main orbitals of all the centers are sensibly perturbed; in particular on the nitrogen we observe either a gain (0.19 e) in the p(E) orbitals or a loss in the s (0.14 e) and $p(A_1)$ (0.3 e) orbitals. Similar variations occur on the carbon atom – *e.g.* the loss of 0.2 e in the p(E) orbitals. The B–N overlap population is smaller than the B–C overlap of the cyanoborohydride (0.36 e) and presents predominant sigma character, although a non-negligible pi participation remains.

At last, we have calculated the geometric (BH optimized = 1.26 Å) and electronic structure of the borohydride ion BH_4^-, and we have compared the results to the electronic structure of the cyanoborohydride ion BH_3CN^-, in order to explain the different chemical behaviour of the two species. Sodium borohydride indeed manifests strong and widely used reducing properties. On the contrary, the corresponding sodium cyanoborohydride is a mild and very selective reducing agent [7] and is therefore highly appreciated in recent organic synthesis [8]. The results of the calculations on BH_4^- are reported in Table IV and are in good agreement with earlier contributions [11]. Mulliken charge is 0.06 e for the boron atom and the unit negative charge of the borohydride ion is distributed among the four H atoms, since the piling up of this charge can be observed in the bond region (B–H overlap population = 0.76 e) and on each hydrogen (–0.27e).

The chemical reducing behaviour of the borohydride can therefore be rationalized by this high localization of the electronic charge, by opposition to the practically neutral hydrogen atoms of the cyanoborohydride; the latter situation is mainly the consequence of the withdrawing effect of the cyano group of the BH_3CN^- ion, and the negative charge is essentially distributed here among the boron (0.53 e) and the nitrogen (0.33 e).

Conclusion

The determination of the geometric and electronic structures of the cyano- and isocyanoborohydride ions BH_3CN^- and BH_3NC^- shows that, in spite of a very similar configuration these compounds present substantial differences in their electronic distribution, in their stability and in the nature of the B–N and B–C bonds.

The highly selective and mild reducing character of these species is explained by an electronic structure in which the hydrogen are discharged, in particular to the help of the boron atom.

The rationalization of the synthesis of the isocyanoborohydride compounds from HCN involves the isomerization of the latter. Conformational analysis of this reaction shows that either intramolecular or intermolecular mechanisms are energetically possible; however, the first model is chemically favored since it is not sensibly disturbed by steric hindrance or molecular association. Finally, it is useful to note that the *ab initio* method used for this purpose is a very good tool since it gives at every moment the image of the energy and of the electronic situation of the system and consequently, the best understanding of the chemical behaviour and strategy of the synthesis.

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