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An ab initio structural study of cyanamide

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Abstract

To obtain an accurate structural description for the cyanamide molecule, we performed ab initio calculations using a series of different basis sets at the self-consistent field and singles and doubles configuration interaction levels. Both the Hartree–Fock and the correlated computations definitely predict a non-linear N≡C–N molecular frame and an inversion barrier around the amido nitrogen atom of 5.7 kJ mol^{-1}, in excellent agreement with microwave experimental results.

Introduction

The present paper reports work on the structural properties of the ground $|^1A'\rangle$ state of the cyanamide molecule as obtained by ab initio Hartree–Fock (HF) and singles and doubles configuration interaction (SDCI) techniques. Cyanamide is a rather interesting species (for industrial interest in cyanamide, see ref. 1) and has been the subject of a number of theoretical [2–14] and experimental [15–25] investigations. The two most important structural features of cyanamide are (a) the energy barrier to nitrogen inversion (IB) and (b) the deviation from linearity of the N≡C–N molecular spine. The question of the non-planarity around the amido nitrogen atom was settled some years ago [9,21]: the equilibrium geometry of the amido nitrogen atom in the gaseous phase is pyramidal with an experimentally determined out-of-plane angle $\tau = 45°$ [23]. Figure 1 defines the geometrical parameters of $N{\equiv}CNH_2$; in particular the out-of-plane angle τ is defined as the angle between the bisector of the HNH angle and the extension of the C–N single bond. Although there is by now no doubt of the pyramidal character of the central nitrogen atom, this question is intimately connected with the magnitude of its IB. Indeed, in the present case it seems that we are dealing with a very low IB: experimental values reported range from 6 kJ mol^{-1} [20,23] to 9 kJ mol^{-1} [21].

The microwave (MW) experimental results of Tyler et al. [21] propose an IB value of 8.5 kJ mol^{-1} for cyanamide, in reasonable agreement with the ab initio self-consistent field (SCF) results of Lehn and Munsch [3], who predict a value of 7.5 kJ mol^{-1}. However, Tyler et al. [21] expressed some doubts as to the validity of their IB and seem to favour the lower value of 5.6 kJ mol^{-1} obtained earlier by Jones and Sheppard [20].

A more recent and very thorough microwave investigation by Brown et al. [23], based on a semirigidbender methodology, suggests that $N{\equiv}CNH_2$ has an IB of 6.1 kJ mol^{-1}. At the same time their analysis definitely indicates that the N≡C–N spine is bent by about 5°, in a trans fashion to the NH_2 plane ($\gamma = 175°$) (Fig. 1). In the earlier analysis of Tyler et al. [21], the N≡C–N

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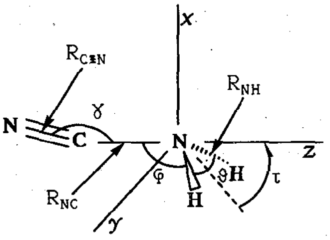

Fig. 1. Definition of geometrical parameters and coordinate frame of the cyanamide molecule.

linkage was assumed linear ($\gamma = 180°$). Interestingly enough, in the molecules of difluorocyanamide $N{\equiv}CNF_2$ (unpublished SCF results from this laboratory [26] predict a skeletal angle $\gamma = 175.5°$ and an IB of $95\,kJ\,mol^{-1}$ for $N{\equiv}C{-}NF_2$) and cyanofluorophosphine $N{\equiv}CPF_2$, which are "isovalent" with cyanamide, non-linearity of the N≡C–N and N≡C–P spines (by about 6° and about 9° respectively) was observed as early as 1972 by Schwendeman and co-workers [27].

It is interesting to note at this point that a slight tilt of the N≡C–N molecular frame, by about 1° was hesitantly suggested in 1976 by Howell et al. [6] through an ab initio SCF study. It is also worth mentioning that an N≡C–N angle has been detected even in the crystalline phase. A careful X-ray diffraction analysis at the low temperature of 108 K [25] reveals a deviation from linearity of about 2° ($\gamma = 178°$). (Cyanamide has a melting point of 46°C, remarkably high for a compound of molecular weight (m.w. = 42); the isoelectronic species $CH_3{-}C{\equiv}N$ (m.w. = 41) and $F{-}C{\equiv}N$ (m.w. = 45) have melting points −46°C and −82°C respectively. Apparently, this is due to the ability of $N{\equiv}C{-}NH_2$ to form a net of intermolecular hydrogen bonds: in the crystalline phase each cyanamide molecule is linked to four neighbouring molecules by two pairs of symmetry-related hydrogen bonds [25]).

The purpose of the present study is to define the geometrical structure of the cyanamide system in greater detail and calculate the magnitude of the energy IB with greater reliability. As far as we know, the only post-HF work in the literature is that of Vincent and Dykstra [8] using the self-consistent electron pairs (SCEP) methodology. These researchers calculate an almost zero IB at the SCF level using a DZ + P basis (Table 1), although they do not mention any correlated IB result. The rest of the existing ab initio results [2–7,9–13] are at the SCF level and use rather limited basis sets.

We have performed ab initio calculations at both the SCF and SDCI levels by increasing the basis set size in a systematic way.

Computational approach

On the C and N atoms we have used Huzinaga's (10s6p) Gaussian basis [28] contracted to [5s4p] according to Dunning [29]. A set of 3d polarization functions was added to C and N atoms with exponents of 0.75 and 0.80 respectively [30]. This basis set was characterized as {1d}. A second basis set named {2d} was constructed by adding two sets of 3d polarization Gaussian functions on C and N atoms [31]. A third basis set symbolized {2d*}, augments the previous {2d} basis by a set of f Gaussian polarization functions, only on the pyramidal nitrogen atom. Finally, the {2d*} basis was augmented by a set of polarization functions of f symmetry for all three heavy atoms. This basis set was named {1f}. All f exponents were arbitrarily set equal to 1.0. Owing to the nature of the Cartesian Gaussian functions, the six d Gaussians form linear combinations which correspond to the traditionally accepted 3d orbitals and one 3s orbital. Similarly, the ten f-type Gaussians produce seven 4f atomic orbitals and three 4p atomic orbitals. No attempt was made to separate the Gaussians into the traditional forms. For the H atom and for all the aforementioned basis sets a (5s) primitive contracted to [3s] was used, augmented by a set of 2p polarization Gaussian functions with an exponent of 1.0 [31]. Collectively, for all bases

$\{1d\}$: $((10s6p1d)_3/(5s1p)_2) \rightarrow [(5s4p1d)_3/(3s1p)_2]$

$\{2d\}$: $((10s6p2d)_3/(5s1p)_2) \rightarrow [(5s4p2d)_3/(3s1p)_2]$

$\{2d^*\}$: $((10s6p2d)_3\,1f_N/(5s1p)_2) \rightarrow$

$[(5s4p2d)_3\,1f_N/(3s1p)_2]$

TABLE 1

Absolute energy (E), equilibrium geometrical properties, energy inversion barrier (IB) and dipole moment (μ) of the ground state of cyanamide as a function of basis set size, in the Hartree–Fock approximation

Property[a]	Basis set						Experiment[b]	
	{1d}[c]	{2d}[c]	{2d*}[c,d]	{1f}[c]	6-31G**[e]	DZ + P[f]	Ref. 21	Ref. 23
$E(+147)$	−0.96323	−0.96888	−0.97128	−0.97416	−0.91683	−0.94030	–	–
R_{NH}	0.998	0.999		0.996	0.996	0.992	1.001	1.008
R_{NC}	1.336	1.343		1.339	1.341	1.336	1.345	1.350
$R_{C\equiv N}$	1.133	1.132		1.130	1.138	1.157	1.160	1.165
ϑ	113.2	113.2		113.5	114.0	116.2	113.3	112.8
φ	114.4	114.2		114.5	114.9	115.0	115.6	113.0
τ	41.4	41.4	41.4	40.5	39.5	37.0	37.6	45.0
γ	178.2	178.0		178.0	178.3	178.2	180.0[g]	174.8
IB[h]	3.2	5.1	3.4	3.9	3.4	0.0	8.5	6.1
μ	4.67	4.69	4.67	4.68	4.62	–	4.32	4.25

[a] Energies in hartree (E_H) bond lengths in Ångströms, angles in degrees, inversion barriers in kilojoules per mole and dipole moments in debyes.

[b] Microwave results.

[c] This work.

[d] Optimization of the out-of-plane angle τ only.

[e] Obtained from ref. 13.

[f] Obtained from ref. 8.

[g] Assumed.

[h] $E_H = 627.51\ \mathrm{kcal\,mol^{-1}}$; 1 cal = 4.184 J.

$$\{1f\}: ((10s6p2d1f)_3/(5s1p)_2) \rightarrow [(5s4p2d1f)_3/(3s1p)_2]$$

The {1f} set contains 166 primitive and 129 contracted Gaussian functions.

For all four basis sets SCF-RHF calculations were carried out. Full geometry optimization under the HF ansatz was performed for all other basis sets except the {2d*}; for the latter the out-of-plane angle τ was varied in conjunction with the {2d} optimal parameters.

SDCI valence correlated calculations were performed using the {1d} and {2d} descriptions. For either the {2d*} or the {1f} basis, SDCI computations were beyond our computing capabilities. For the {1d} basis no geometry optimization was done at the configuration interaction (CI) level; simply the {2d} SCF geometry was used. At the {2d} CI level the most important parameters were optimized, namely the $R_{C\equiv N}$ bond length, the out-of-plane angle τ and the spine angle γ. For the other geometrical parameters the {2d} SCF optimal parameters were used.

All computations were done with Davidson's set of codes MELDF [32]. The SCF-RHF computations were performed on the microVAX-3300 of our laboratory, and the SDCI calculations were carried out on the VAX-9000 of the University of Thessaloniki.

Results and discussion

Tables 1 and 2 condense most of our results. Table 1 presents, for reasons of comparison, along with our SCF values, two sets of SCF results from the literature [8,13], and experimental MW results [21,23]. The particular theoretical results taken from the literature were chosen because they appear to be the best as far as their absolute SCF energies are concerned. The relatively recent experimental MW results of Brown et al. [23], obtained via semirigidbender analysis, are more

TABLE 2

Absolute Energy (E), bond lengths, angles, IB and dipole moment (μ) of the ground state of cyanamide as obtained by the SDCI (SCF + 1 + 2) method; only the geometrical parameters indicated have been optimized, the others are those of column {2d} of Table 1

Method[a]	E (hartree)	$R_{C\equiv N}$ (Å)	ϑ (deg)	τ (deg)	γ (deg)	IB (kj mol^{-1})	μ (D)
SDCI{1d} (≈82 000)	−148.40162[b]					4.10[b]	4.51[b]
SDCI{2d} (≈129 000)	−148.43380	1.147	113.9	42.7	177.3	5.67	4.56
SDCI{2d} + Davidson[c]						6.6	

[a] The notation {1d}, {2d} refers to the corresponding basis set employed; the numbers in parentheses refer to the size of the CI.
[b] No geometry optimization; the Hartree–Fock {2d} geometry was used.
[c] Davidson's correction ($\Delta E_Q = (1 - \mathrm{Co}^2)\ E_{\mathrm{corr}}$ (SDCI) [33]) was taken into account.

realistic than the earlier results of Tyler et al. [21]. Yet, because our theoretical approach is based on the static clamp-nuclei approximation it is fair to contrast our results with those of Tyler et al. [21]. The angle γ in the analysis of Tyler et al. [21] has been assumed equal to 180°, and their energy IB value has been overestimated (vide supra).

The theoretical IB values in Tables 1 and 2 are obtained by taking energy differences of optimized (or semioptimized in the case of the SDCI {2d} calculation) geometries C_s and C_{2v} respectively, i.e.

$$IB = E(|^1A_1\rangle) - E(|^1A'\rangle)$$

where

$$|^1A'\rangle = 1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 8a'^2 9a'^2 1a''^2 2a''^2$$

is the ground state configuration of cyanamide, and $|^1A_1\rangle$ the "ground state" in the C_{2v} symmetry. Note that with a planar geometry of the amido nitrogen atom, there is no a priori reason for the angle γ to be different from 180°. Therefore the molecule necessarily inverts through C_{2v} symmetry.

One would expect the calculated properties to converge towards a certain value as the basis set size increases with concomitant energy lowering. However, as seen in Table 1, we observe no significant variation in the structural parameters as the basis set improves from {1d} to {1f}. Even the calculated dipole moments remain practically independent of the basis set size and in acceptable agreement with the experimental value(s). Only the {2d} basis gives a significant, but rather fortuitous improvement of the calculated IB compared with experimental value(s). This can only mean that the {1d} basis set is already adequately describing the cyanamide system within the HF picture. It is interesting that the split-valence 6-31G** results of Riggs and Radom [13] are in close overall agreement with our {1f} SCF results, whereas the more extended, at least with respect to energy, DZ + P results of Vincent and Dykstra [8] predict an almost zero barrier to inversion (Table 1).

The structural predictions from Table 1 are in keeping with the conventional wisdom of the HF approximation: owing to a complete lack of dynamical correlation, which results in charge accumulation between the bonded regions, bond lengths are calculated shorter by as much as 0.03 Å (see, for instance, $R_{C\equiv N}$), whereas angles are, in general, calculated larger by a few degrees, compared with experiment.

Table 2 presents our SDCI {1d} and {2d} values. The coefficient of the HF configuration in the SDCI expansions, C_{HF}, is very dominant ($C_{HF} = 0.94$), clearly indicating why cyanamide is well described within the HF approximation, as is also evident from Table 1. From Table 2, it is observed that the $R_{C\equiv N}$ bond length has improved substantially, yet it is still shorter by 0.013 Å compared with the MW results of Tyler et al. [21] or by 0.018 Å compared with the results of Brown et al. [23]. This is certainly due to the limited {2d} basis used in our

CI expansion. The out-of-plane angle τ is in good agreement with the results of Brown et al. [23], but deviates by as much as 5° from the results of Tyler et al. [21]. We can also claim that the spine angle γ is now in acceptable agreement with experiment (Table 1), taking into consideration the very small absolute value of this parameter. As far as the dipole moment is concerned, although it is still overestimated by 6–7% compared with experiment [21,23], it has improved significantly over the HF results (Table 1).

Finally, as is shown by Table 2, our IB value is in excellent agreement with the results of Brown et al. [23], the difference between the experimental and the theoretical values being about $0.4\,\mathrm{kJ\,mol^{-1}}$. Taking into consideration Davidson's correction for unlinked clusters [33] the IB result remains of the same numerical character.

Concluding remarks

Our comparison of the ab initio structure of cyanamide with the gas phase experimental MW results (Tables 1 and 2) shows good overall agreement. In particular, our calculations clearly indicate that the molecular frame N≡C–N deviates from linearity by about 3°, and the calculated energy inversion barrier of about $6\,\mathrm{kJ\,mol^{-1}}$ is in excellent agreement with the experimental MW results given in the literature [20,23].

The question of why the skeletal angle γ varies from 180° is essentially rhetorical, given the pyramidal character of the amido nitrogen atom. However, cyanamide's very low IB compared with other molecules of the type $X{-}NH_2$ (where X = H, F, Cl and Br) is quite interesting.

The experimental IBs of NH_3, NH_2F and NH_2Cl are $24.2\,\mathrm{kJ\,mol^{-1}}$ [34], $62.2\,\mathrm{kJ\,mol^{-1}}$ [35] and $47.8\,\mathrm{kJ\,mol^{-1}}$ [36] respectively. For NH_2Br we estimate via scaled AM1 semiempirical computations [37] an IB of about $30\,\mathrm{kJ\,mol^{-1}}$ (the average value of the ratios of experimental to AM1 calculated IB values, for the other three molecules yields a scaling factor of 1.23). These four IB values, with a deviation of less than 10% follow the relation

$$\mathrm{IB} = 22(\chi^{\mathrm{P}} - 1)\mathrm{kJ\,mol^{-1}}$$

where χ^{P} is Pauling's electronegativity (see, for example, ref. 38) for H, F, Cl and Br. Accepting an effective (group) electronegativity for the cyano moiety of about 3.8 (see, for example, ref. 38); the above relation fails dismally in predicting the IB of cyanamide. This we take to mean that electronegativity is not the leading factor in dictating the IB of cyanamide and related species. It is rather the ability of the occupied $\approx \pi p_z$ orbital of the central nitrogen atom to back-bond with the available molecular space along the inversion path. This is also the case in aniline ($C_6H_5{-}NH_2$) with an energy IB of $6.3\,\mathrm{kJ\,mol^{-1}}$ [39], very similar to that of cyanamide.

We are at present studying in detail energy IBs and general structural questions in molecular systems of the type $N{\equiv}C{-}YX_2$ (where Y = N, P and X = H, F, Cl and possibly Br) with ab initio quantum chemical methods.

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