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Ab initio investigations of some molecular complexes containing hydrogen cyanide: hydrogen-bonded or donor–acceptor?

L.J. Millar, T.A. Ford*

Centre for Theoretical and Computational Chemistry, School of Chemistry, University of KwaZulu-Natal, Durban 4041, South Africa

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Abstract

The structures, interaction energies and vibrational spectra of some molecular complexes of hydrogen cyanide with several oxygen, nitrogen and halogen compounds have been studied at the correlated level, using a triple zeta basis set with diffuse and polarization functions on all atoms. The partner molecules were chosen in order to investigate whether the structures of the complexes were of the hydrogen-bonded type, in which hydrogen cyanide acts as the proton donor, or of the electron donor–acceptor type, in which it plays the rôle of the electron donor. The computed properties of the complexes have been correlated with the nature of the partner molecule and are shown to form a consistent set of data which successfully describes the perturbations of the properties of the hydrogen cyanide monomer species as it undergoes formation of molecular complexes with other small molecules.

Keywords: Ab initio; Molecular complexes; Hydrogen bonding; Hydrogen cyanide; Interaction energies; Vibrational spectra

1. Introduction

The use of ab initio molecular orbital theory to predict the properties, such as the structures, interaction energies and vibrational spectra of molecular complexes is now well-established [1]. We have used this technique in our studies of a number of series of adducts, of the hydrogen-bonded (HB) [2,3], electron donor–acceptor EDA [4,5] and van der Waals (VDW) [6,7] types. Among the various associated species featured in these reports we have determined the properties of the complexes of hydrogen cyanide with water [8] and with boron trifluoride [9,10]. In the first of these, the complex is stabilized by a CH···O hydrogen bond, with hydrogen cyanide acting as the proton donor and water as the acceptor. In the second, the interaction is of the EDA type, with the nitrogen lone pair orbital of hydrogen cyanide (5σ) donating electronic charge to the vacant $2a_2''$ molecular orbital of boron trifluoride which correlates with the axial $2p_z$ atomic orbital of boron. These examples illustrate two of the ways in which hydrogen cyanide may interact with a partner molecule in the formation of a molecular complex. In this paper, we explore a series of complexes containing hydrogen cyanide with a number of other small molecules, in an attempt to determine the preferred method of interaction employed in each case, and in so doing to reveal the rules which govern the molecular structures and vibrational properties of these aggregates. The partner molecules investigated in this work include three oxygen (SO_2, H_2CO and CO_2), two nitrogen (N_2 and FCN), three halogen (FCN, F_2 and BF_3) and one carbon-containing species (CO). Some of these molecular complexes have been previously investigated spectroscopically in the gas phase [11–23].

2. Computational method

The computations were carried out using the GAUSSIAN-98 molecular orbital computer package [24], at the second-order level of Møller–Plesset perturbation theory (MP2) [25], with the 6-311++G(d,p) basis set [26,27]. Full geometry optimizations were carried out, imposing only the molecular symmetry determined to correspond with the local minima on the various potential energy surfaces. The tightest available convergence criterion was used in each

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* Corresponding author. Tel.: +27 312601096; fax: +27 312603091.
E-mail address: ford@ukzn.ac.za (T.A. Ford).

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case. Interaction energies were calculated by subtraction, and were corrected for basis set superposition error (BSSE) [28] using the full Boys–Bernardi counterpoise technique [29]. Normal coordinate analysis was applied to identify the stationary points and to distinguish genuine minima from saddle points, and led to values of the wavenumbers and infrared intensities of the modes of the complexes. These were then used to calculate the complex-monomer wavenumber shifts and the infrared band intensity ratios. These parameters for the CH stretching modes of the HB complexes were then correlated with some properties of the proton acceptors (the proton affinity and the ionization energy) which determine the nature and strength of the interaction. For the EDA complexes, the critical spectroscopic property is the wavenumber shift of the CN stretching mode, and these shifts were correlated with the electron affinities of the electron acceptors.

3. Results and discussion

3.1. Molecular structures

Table 1 presents a summary of the results obtained, listed as the preferred structure of each complex, its molecular symmetry, and its corrected interaction energy. Hydrogen cyanide forms linear CH$\cdots$N (**1**) and CH$\cdots$C (**2**) HB complexes with the diatomic molecules N_2 and CO, in agreement with experiment [11,13,16,17]. The electron donor orbitals are the $3\sigma_g$ (non-bonding N) of N_2 and the 5σ (non-bonding C) of CO. Attempts to achieve convergence in a perpendicular EDA structure, with a N atom of N_2 interacting with the central C atom of HCN, resulted in the adduct yielding a slightly non-planar structure with a N$\cdots$C interaction, but which was found to be a saddle point. In the case of the corresponding perpendicular C$\cdots$C bound EDA complex of HCN and CO, the adduct dissociated into the separate molecules. In contrast, the complex with F_2 converged to a HB structure of C_s symmetry (**3**) with a H$\cdots$FF angle of about 78°, and also yielded a linear N$\cdots$F bound complex (**4**) when starting from an EDA aggregate structure, in agreement with the structure established spectroscopically by Cooke et al. [23]. The HB complex is stabilized by donation from the $1\pi_g$ non-bonding orbital of F_2, explaining the fact that the complex is L-shaped, rather than linear. In the case of the EDA complex, donation takes place from the 5σ N lone pair orbital of HCN to the vacant axial $3\sigma_u$ antibonding orbital of F_2. The preferred complex with CO_2 was found to be of the EDA type, featuring a N$\cdots$C interaction in a perpendicular structure (**5**), with the N lone pair of HCN interacting with the CO_2 $2\pi_u$ antibonding orbital centred mainly on the C atom [12, 18–20]. An alternative linear NCH$\cdots$OCO HB model was found to converge only when constrained to a $C_{\infty v}$ structure, and then only as a second-order saddle point, although there is some experimental evidence for the existence of this linear structure [18,20]. The linear HB structure is disfavoured by the fact that the HOMO of CO_2 is the $1\pi_g$ non-bonding O orbital, which is of course non-axial. In the case of the complex with FCN two HB models, one involving a CH$\cdots$N and the other a CH$\cdots$F interaction, were examined. In the first case the donor orbital is the 5σ non-bonding N, and in the second the 1π non-bonding F, which would lead to a non-linear species. The first structure (**6**) converged, but the second relaxed to an antiparallel EDA complex (**7**), which was also found to be a genuine minimum. In addition, a second, linear, EDA aggregate with a N$\cdots$F interaction (**8**), was found to be a true minimum, in which donation occurs from the 5σ non-bonding N orbital of HCN to the vacant axial 8σ CF antibonding orbital of FCN.

Table 1
Summary of the preferred structures, point group symmetries and corrected interaction energies of some stable complexes of hydrogen cyanide[a]

Partner molecule	Hydrogen-bonded		Electron donor–acceptor	
	Symmetry	ΔE/ kJ mol^{-1}	Symmetry	ΔE/ kJ mol^{-1}
N_2	$C_{\infty v}$ (**1**)	−4.896	–[b]	–
CO	$C_{\infty v}$ (**2**)	−6.978	–[b]	–
F_2	C_s (**3**)	−0.785	$C_{\infty v}$ (**4**)	−3.165
CO_2	–[b]	–	C_{2v} (**5**)	−6.491
FCN	$C_{\infty v}$ (**6**)	−16.114	C_s (**7**)	−9.055
			$C_{\infty v}$ (**8**)	−3.850
SO_2	C_s (**9**)	−9.855	C_s (**10**)	−10.856
BF_3	C_{2v} (**12**)	−4.795	C_{3v} (**11**)	−20.654
H_2CO	C_s (**13**)	−16.128	C_s (**14**)	−12.241

[a] Bold numbers in parentheses refer to descriptions of complexes (see text).

[b] Failed to converge.

The complexes formed between HCN and SO_2 were a HB CH$\cdots$O structure (**9**) with a *trans* H$\cdots$OSO fragment—here the electron donor orbital is the $5b_2$ non-bonding O orbital of SO_2—and a N$\cdots$S bound EDA adduct (**10**) having N$\cdots$SO angles of about 92°, in which the HCN 5σ orbital donates charge to the vacant $3b_1$ π antibonding orbital of SO_2. A *cis* H$\cdots$OSO HB structure was found to be a saddle point. Goodwin and Legon have reported a structure similar to **10** in the gas phase, but were unable to find any evidence for the alternative HB complexes [14]. The HCN·BF_3 complex has been well-characterized experimentally, as a C_{3v} N$\cdots$B bound EDA aggregate (**11**) [21,22]. Donation is from the HCN 5σ orbital to the $2a_2''$ orbital of BF_3. We have also found a second, HB, isomer (**12**) with a linear CH$\cdots$F interaction, in a C_{2v} structure in which the donor orbital is the $1a_2'$ non-bonding F orbital, but there is no experimental evidence to support this. Hydrogen cyanide forms two stable complexes with H_2CO, a linear C_s HB species (**13**) with a CH$\cdots$O hydrogen bond and a H$\cdots$OC angle of about 135°, and an EDA structure (**14**) stabilized by both a CH$\cdots$O and a CH$\cdots$N interaction. The HB species features proton