Journal of Molecular Structure 967 (2010) 1–14

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Structural parameters, vibrational spectra and centrifugal distortion constants of F(CN)C=NX (X = H, F, Cl, Br) and CH_3(Y)C=NH (Y = H, CN)

James R. Durig *, Sarah Xiaohua Zhou [1], Carmen Xiaomin Zhou, Nicole E. Durig

Department of Chemistry, University of Missouri–Kansas City, Kansas City, MO 64110, USA

ARTICLE INFO

Article history:
Received 5 November 2009
Accepted 2 December 2009
Available online 8 February 2010

Keywords:
Ab initio calculations
r_0 structural parameters
F(CN)C=NX (X = H, F, Cl, Br) molecules
Iminopyruvonitrile
Ethylidenimine

ABSTRACT

Ab initio calculations with full electron correlation by the perturbation method to second order and hybrid density functional theory calculations by the B3LYP method utilizing a variety of basis sets have been carried out for the F(CN)C=NX (X = H, F, Cl, Br) and CH_3(Y)C=NH (Y = H, CN) molecules. From these calculations, force constants, vibrational frequencies, infrared intensities, Raman activities, depolarization ratios, and structural parameters have been determined and compared to the experimental quantities when available. By combining previously reported rotational constants for F(CN)C=NBr with the *ab initio* MP2/6-311+G(d) predicted parameters, adjusted r_0 parameters have been obtained. The structural parameters are: distances (Å) (N–Br) = 1.865(3); (C=N) = 1.270(3); (C–F) = 1.327(3); (C–C) = 1.437(3); (C≡N) = 1.160(3); and angles (°) ∠BrNC = 114.4(5); ∠NCF = 127.4(5); ∠NCC = 119.7(5). These reported parameters have much lower uncertainties than those previously reported from the microwave data. Similar theoretical calculations have been carried out for CH_3(Y)C=NH (Y = H, CN) and r_0 structural parameters have been obtained for both the *cis* and *trans* conformers of ethylidenimine, CH_3(H)C=NH, and for *cis* iminopyruvonitrile, CH_3(CN)C=NH utilizing previously reported microwave rotational constants. For CH_3(H)C=NH the determined r_0 heavy atom parameters for the *cis* [trans] form are: distances (Å) (C=N) = 1.276(3) [1.275(3)]; (C–C) = 1.500(3) [1.508(3)]; angles (°) ∠(HN=C) = 109.4(5) [108.8(5)]; ∠(N=CC) = 121.2(5) [127.2(5)]; ∠(HCC) = 116.2(5) [116.4(5)]. Centrifugal distortion constants have been obtained for all of the molecules from the *ab initio* predicted force constants and the values are compared to the experimentally determined values when available. The results of these studies are compared to the corresponding quantities of some other similar molecules.

1. Introduction

We recently carried out structural and vibrational studies of F_2C=NX (X = H, F, Cl, Br) and compared the experimentally determined values for the structural parameters and fundamental frequencies to those predicted from *ab initio* and density functional theory (DFT) calculations [1]. By comparing previously reported rotational constants [2–4] for all four F_2C=NX molecules with *ab initio* MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters were obtained. The r_0 values for F_2C=NH and F_2C=NF were in excellent agreement with previously determined [2,3] values except for the difference in the two CF distances of F_2C=NH which differ by 0.017 Å compared to the 0.008 Å estimated value. However, for the chloride and bromide the newer determined values had much lower uncertainties of 0.005 Å for the NX distances and 0.003 Å for the C=N distances compared to the earlier reported [5] uncertainties of 0.031 and 0.016 Å for the NCl(Br) and C=N distances, respectively, from the microwave data alone. Similar improvements for several of the angles such as CF_2, F_cCN, and CNX with uncertainties of 3.1°, 2.6°, and 1.8°, respectively, were improved with uncertainties of 0.5°. Since there is very limited structural data available for NCl and NBr bond lengths for trigonal bonded molecules in the gas phase we have continued to carry out structural and vibrational studies of substituted *N*-halomethanimine F(CN)C=NX (X = H, F, Cl, Br). For comparison purposes we have also investigated iminopyruvonitrile, CH_3(CN)-C=NH, where microwave data [6] are available as well as ethylidenimine, CH_3(H)C=NH, where the microwave data [7] for both the *cis* and *trans* conformers are available. The results of these investigations are reported herein.

2. Theoretical calculations

In order to provide vibrational frequencies with both infrared and Raman intensities and optimized geometries, *ab initio* calculations were carried out by using the Gaussian-03 program [8] by the

* Corresponding author. Tel.: +1 816 235 6038; fax: +1 816 235 2290.
E-mail address: durigj@umkc.edu (J.R. Durig).

[1] Taken in part from the dissertation of S.X. Zhou which will be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. Degree.

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.12.004

perturbation method to second order (MP2) with full electron correlation [9]. Two basis sets, 6-31G(d) and 6-311+G(d), have been utilized. DFT calculations have also been carried out by the B3LYP method by utilizing the 6-311+G(d) basis set. Frequencies for the fundamentals have been predicted for both the *trans* and *cis* conformers for all six molecules along with the predicted infrared intensities and Raman activities and these data are listed in Tables 1 and 2, respectively, for the F(CN)C=NX (X = H, F, Cl, Br) molecules and in Tables 3 and 4, respectively, for CH_3(CN)C=NH and CH_3(H)C=NH.

In order to obtain a complete description of the molecular motions involved in the normal modes, the force field in Cartesian coordinates was calculated with the 6-31G(d) and 6-311+G(d) basis sets at the MP2 level as well as with 6-311+G(d) basis set from the hybrid DFT calculations by the B3LYP method. The internal coordinates for the F(CN)C=NX (X = H, F, Cl, Br) molecules were the five bond distances, the four planar angles, and the three dihedral angles. The B matrix was used to convert the *ab initio* force field in Cartesian coordinates to a force field in internal coordinates [10].

To show the differences in the predicted and observed spectra for the F_2C=NX (X = H, F, Cl, Br) molecules we calculated the theoretical infrared and Raman spectra. The calculated frequencies, infrared intensities, and Raman scattering activities were obtained from both the *ab initio* and hybrid DFT calculations. Infrared intensities were calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the *ab initio* calculation and transformed to the normal coordinates by $(\partial\mu_u/\partial Q_i) = [\Sigma(\partial\mu_u/\partial X_j]L_{ij}$, where Q_i is the ith Cartesian displacement coordinate, L_{ij} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by: $I_i = [(N\pi)/(3c^2)][(\partial\mu_x/\partial Q_i)^2 + (\partial\mu_y/\partial Q_i)^2 + (\partial\mu_z/\partial Q_i)^2]$.

The evaluation of the Raman activity by using the analytical gradient method has been developed [11,12] where the activity, S_j, can be expressed as: $S_j = g_j(45\alpha_j^2 + 7\beta_j^2)$ and g_j is the degeneracy of the vibrational mode j, α_j is the derivative of the isotropic polarizability, and β_j is that of the anisotropic polarizability. The Raman scattering cross sections, which are proportional to the Raman intensities, can be calculated from the scattering activities [13,14]. To obtain the polarized Raman cross sections, the polarizabilities are incorporated into S_j by multiplying S_j with $(1-\rho_j)/(1+\rho_j)$, where ρ_j is the depolarization ratio of the jth normal mode. The Raman scattering cross sections and the calculated frequencies were used together with the Lorentzian function to obtain the calculated spectrum.

3. Vibrational spectra and structural parameters

3.1. Fluorocyanomethanimine (F(CN)C=NH)

Of the four molecules with F(CN)C=N moiety only the vibrational spectra of *N*-chloro and *N*-bromo molecules been reported from which the predicted spectra can be compared. Therefore for the imine and *N*-fluoro molecules the predicted spectra for both the *trans* and *cis* conformer will be compared for both the infrared and Raman spectra which should aid in identifying their spectra if or when these molecules are prepared and evidence is needed for their identification. Since the infrared spectra of both the gaseous *N*-chlorofluorocyanomethanimine and *N*-bromofluorocyanomethanime have been reported it will be possible to compare them with the predicted ones as well as those of F(CN)C=NH and F(CN)C=NF. Thus, we have obtained the frequencies for the fundamentals of F(CN)C=NH by *ab initio* MP2(full)/6-31G(d) and MP2(full)/6-311+G(d) calculations as well as with density functional theory by the B3LYP method (Table 1). Except for the C≡N stretching vibration, the heavy atom stretching frequencies (Table 1) predicted from the MP2(full)/6-31G(d) calculations were obtained by scaling the force constants by 0.90 and frequencies with this scaling factor have been used for making Fig. 1 as well as the figures for the other molecules. Also in Fig. 1 are the predicted spectra from the B3LYP/6-311+G(d) calculations.

As can be seen from the spectrum in Fig. 1A (*cis* F(CN)C=NH) with that in Fig. 1C (*trans* form) there is little difference except below 900 cm^{-1} where the FCC symmetric stretch for the *cis* form is predicted to be about one tenth the intensity of the corresponding fundamental for the *trans* conformers. Also, the A" FCC bend for the *trans* form will probably not be observed (predicted intensity of 0.1 km/mol) whereas this vibration for the *cis* form has a predicted intensity of 7.6 km/mol. Also, the predicted intensities for the two lowest frequency modes (CC≡N bends) for the *cis* form are significantly larger than those for the *trans* conformer whereas the FCC wag of the *trans* is about six times stronger than the corresponding mode for the *cis* conformer. These differences should make it easy to distinguish between the two forms (Fig. 1). However, there is very little difference (Fig. 1D, *trans* and Fig. 1F, *cis*) between the two Raman spectra of these conformers except for the FCC mode which is slightly weaker for the *cis* form. Finally, there is a large frequency and activities difference for the C≡N and C=N modes predicted for the Raman spectra from the MP2 calculations (Fig. 1D) versus those from the B3LYP calculations (Fig. 1E) for the *trans* conformer. These differences are mainly due to the much shorter predicted bond length for the C≡N and C=N bonds by the B3LYP calculations which are approximately the experimentally determined values.

There is significant mixing with most of the modes where the vibration assigned as the N–H bend is only 47% of S_4 with 30% S_5 (FCC antisymmetric stretch) and 17% S_8 (FCC wag). This mixing continues with the FCC antisymmetric stretch where the P.E.D. for the *trans* form has 50% S_5 and 41% S_4 (N–H bend). However, for the *cis* conformer the contribution from these two symmetry coordinates is reversed with the FCC antisymmetric stretch having 41% S_5 and 54% S_4 of the N–H bend. Also the FCC scissor (S_7) and FCC wag (S_8) have contributions from three different symmetry coordinates. Even in the A″ symmetry block there is significant mixing between the FCC bend and the CC≡N bend. Nevertheless, the appropriate descriptions given to the rest of the vibrations have major contribution.

Based on the predicted energy difference of 29 cm^{-1} (0.35 kJ/mol) from the MP2/aug-CC-PVTZ calculations (Table 5) between the more stable *trans* form and the less stable *cis* conformer there should be nearly 45% of the *cis* form present at ambient temperature based on the energy difference. However, the *cis* form would not be expected to exchange with the *trans* conformer since the energy barrier for the N–H inversion is predicted to be 7522 cm^{-1} (90.0 kJ/mol) from the MP2(full)/6-31G(d) calculations. Nevertheless if it were prepared it should remain as the *cis* form and it should be possible to distinguish it from the *trans* conformer by its vibrational spectrum.

The structural parameters have been obtained from MP2(full)/6-311+G(d) and B3LYP/6-311+G(d) calculations for *trans* F(CN)C=NH (Table 6) and we have estimated r_0 parameters based on the differences expected from the *ab initio* and DFT calculations. For example MP2 calculations with the 6-311+G(d,p) basis set predicts triple bond distances about 0.015 Å too long and the double bonds are also predicted too long. Therefore the C≡N distance is predicted to be 1.156 Å compared to the MP2 value of 1.175 Å and the predicted C=N distance is between the values from the MP2 and B3LYP calculations. Some very small adjustments were made on a few of the angles based on values for these angles obtained from the adjusted r_0 parameters for the F_2C=NX (X = H, F, Cl, Br)