Conformational stability from variable temperature FT-IR spectra of xenon solutions and ab initio calculations of trans 3-pentenenitrile and 3-methyl-3-butene nitrile

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · MAY 2001

4 AUTHORS, INCLUDING:

Gamil A. Guirgis
College of Charleston
341 PUBLICATIONS **2,686** CITATIONS

Conformational stability from variable temperature FT-IR spectra of xenon solutions and ab initio calculations of *trans* 3-pentenenitrile and 3-methyl-3-butene nitrile

G.A. Guirgis, S. Shen, B.R. Drew, J.R. Durig*

Department of Chemistry, University of Missouri-Kansas City, 5100 Rockhill Road, Kansas City, MO 64110-2499, USA

Abstract

The infrared (3500–40 cm^{-1}) spectra of gaseous, liquid and solid 3-methyl-3-butene nitrile, $CH_2C(CH_3)CH_2CN$, and *trans* 3-pentenenitrile, $CH_3CHCHCH_2CN$, have been recorded. Both the *cis* and *gauche* conformers have been identified for both conformers in the fluid phases but only the *cis* form remains in the solid. Variable temperature (−55 to −100°C) studies of the infrared spectra of the samples dissolved in liquid xenon have been carried out. From these data, the enthalpy difference has been determined to be 174 ± 20 cm^{-1} (2.08 ± 0.24 kJ/mol) for 3-methyl-3-butene nitrile with the *cis* conformer the more stable rotamer and 187 ± 20 cm^{-1} (2.23 ± 0.24 kJ/mol) for *trans* 3-pentenenitrile, again with the *cis* rotamer the more stable form. Complete equilibrium geometries have been obtained for both rotamers for both molecules by ab initio calculations employing the 6-31G(d), 6-311G(d,p), 6-311 + G(d,p) and 6-311 + G(2d,2p) basis sets at the levels of restricted Hartree–Fock and/or Moller–Plesset to second order. Only the MP2/6-311 + G(2d,2p) calculation gives the correct conformer stability for 3-methyl-3-butene nitrile. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Conformational stability; Infrared and Raman spectra; 3-Methyl-3-butene nitrile; *trans* 3-Pentenenitrile

1. Introduction

We previously investigated the conformational equilibria exhibited by 3-butenenitrile [1,2] (allyl cyanide) (CH_2=$CHCH_2CN$), and determined that the *cis* (cyano group is eclipsing the double bond) conformer is the more stable rotamer in the liquid phase and the only form remaining in the solid. From the more recent study [2], a variable temperature investigation of the infrared spectrum of the sample dissolved in liquid xenon was carried out.

From these data it was concluded that the enthalpy value was 336 ± 61 cm^{-1} (4.02 ± 0.73 kJ/mol) with the *cis* conformer the more stable rotamer. This enthalpy value should be near that for the gas [3–7]. In order to determine the effect of substitution of a methyl group on the ethylene moiety of 3-buteni-trile we have investigated the conformational stability of 3-methyl-3-butene nitrile, $CH_2C(CH_3)CH_2CN$, and *trans* 3-pentenenitrile, $CH_3CHCHCH_2CN$, utilizing variable temperature infrared spectra of xenon solutions of these two molecules. In order to assign the individual bands to the correct conformers we have carried out MP2/6-31G(d) ab initio calculations utilizing scaling factors of 0.88 for the carbon–hydrogen stretches, 0.90 for the carbon–hydrogen

* Corresponding author. Tel.: +1-816-235-1136; fax: +1-816-235-5502.

  E-mail address: durigj@umkc.edu (J.R. Durig).

Table 1
Temperature and intensity ratios from the conformational study of
trans 3-pentenenitrile and 3-methyl-3 butene nitrile

T (°C)	1000/T (K)	CH$_3$CHCHCH$_2$CN $-\ln(I_{883}/I_{839})$	CH$_2$C(CH$_3$)CH$_2$CN $-\ln(I_{551}/I_{570})$
−55	4.58	1.281	0.115
−60	4.69	1.281	0.110
−65	4.80	1.337	0.068
−70	4.92	1.369	0.033
−75	5.05	1.392	0.007
−80	5.18	1.431	−0.039
−85	5.31	1.456	−0.063
−90	5.46	1.506	−0.088
−95	5.61	1.545	−0.142
−100	5.78	1.591	−0.164
ΔH (cm^{-1})		187±20	174±20

bends and skeletal stretches, and 1.0 for the skeletal bends and asymmetric torsion. Additionally, complete equilibrium geometries have been obtained for both rotamers for both molecules employing a variety of basis sets with full electron correlation by the perturbation method [8] to second order in order to predict the conformational stabilities.

2. Experimental

A sample of 3-methyl-3-butene nitrile was prepared by the reaction of neat 3-chloro-2-methyl propene
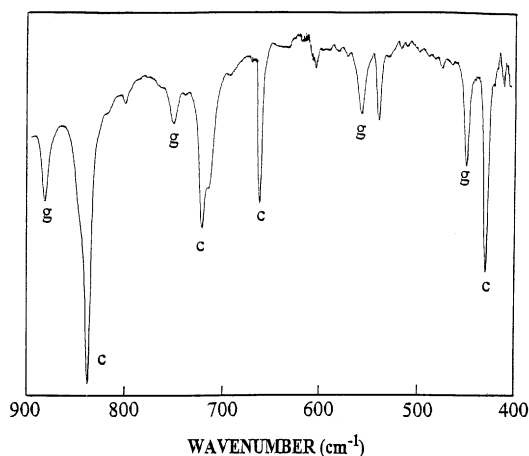

Fig. 1. Infrared spectrum (900–400 cm^{-1}) of *trans* 3-pentenenitrile in liquid xenon.

with sodium cyanide at 150–160°C for 1 h. A sample of *trans* 3-pentenenitrile was prepared by the reaction of neat crotyl chloride with sodium cyanide at 150–160°C. The samples were collected under vacuum and then purified with a low-temperature, low-pressure fractionation column.

The mid-infrared spectra of the samples dissolved in xenon as a function of temperature were recorded on a Bruker model IFS 66 Fourier transform interferometer equipped with a Globar source, a Ge/KBr beamsplitter and a DTGS detector. The spectra were recorded at variable temperatures ranging from −55 to −100°C. All the spectra were collected with 100 scans at a resolution of 1.0 cm^{-1}. The temperature dependent spectral data for the conformer bands are listed in Table 1.

3. Results and discussion

The LCAO-MO-SCF restricted Hartree–Fock (RHF) calculations were performed with the GAUSSIAN-98 program [9] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all of the geometric parameters consistent with the symmetry restrictions using the gradient method of Pulay [10]. The structural optimization for both the *cis* and the *gauche* conformers were carried out with initial parameters taken from those of 3-butenenitrile [2]. The 6-31G(d), 6-311G(d,p), 6-311 + G(d,p) and 6-311 + G(2d,2p) basis sets were employed at the level of RHF and/or Moller–Plesset (MP2) to second order with full electron correlation. For the *trans* 3-pentenenitrile molecule, all of the calculations at the MP2 level predict the *cis* conformer to be the more stable rotamer. However, the value is rather small until the 6-311 + G(2d,2p) basis set is utilized which gives an energy difference of 182 cm^{-1} (2.18 kJ/mol) (Table 2). The infrared spectrum (400–900 cm^{-1}) of the sample dissolved in liquid xenon is shown in Fig. 1 and the peaks at 883, 752, 556 and 449 cm^{-1} are predicted as bands due to the *gauche* conformer at 877, 733, 538 and 435 cm^{-1}, respectively. All of these bands disappear from the spectrum of the annealed solid. From these data it is concluded that the *cis* conformer is the rotamer that remains in the solid state. Also it should be noted that

Table 2
Predicted total energies (Hartree) and energy differences (cm^{-1}) for the two stable conformers of *trans* 3-pentenenitrile and 3-methyl-3-butene nitrile

Method/basis set	*trans* 3-pentenenitrile			3-methyl-3-butene nitrile		
	Energy (*cis*)	Energy (*gauche*)	Energy (cm^{-1})	Energy (*cis*)	Energy (*gauche*)	Energy (cm^{-1})
RHF/6-31G(d,p)	−247.842160	−247.842440	61 (*gauche*)	−247.841582	−247.841807	49 (*gauche*)
MP2(full)/6-31G(d,p)	−248.661536	−248.661200	74 (*cis*)	−248.662702	−248.662998	65 (*gauche*)
MP2(full)/6-311G(d,p)	–	–	–	−248.886790	−248.887240	99 (*gauche*)
MP2(full)/6-311+G(d,p)	−248.892294	−248.892225	15 (*cis*)	−248.893842	−248.894667	181 (*gauche*)
MP2(full)/6-311+G(2d,2p)	−248.959332	−248.959103	182 (*cis*)	−248.962170	−248.962050	−26 (*cis*)

the bands assigned as fundamentals of the *gauche* conformer are less than one-half the intensity of the corresponding bands for the *cis* form. For example, the 427 cm^{-1} band which is assigned as the C=C–C bend has twice the intensity of the 449 cm^{-1} band for the corresponding mode of the *gauche* conformer. Since there are two equivalent *gauche* conformers and the predicted intensities (0.4 km/mol) in the infrared spectra are nearly the same, these relative intensities are a strong indication that the *cis* form is the more stable conformer.

In order to determine the enthalpy difference, ΔH, between the conformers of *trans* 3-pentenenitrile, the relative intensities of the 883 (*gauche*) and 839 (*cis*) conformer doublet were measured as a function of temperature from −55 to −100°C. The results are summarized in Table 1 and show that the intensities of the *cis* band increases, as the temperature is decreased compared to the intensities of the *gauche*

band. Utilizing the van't Hoff equation, $-\ln K = (\Delta H/RT) - (\Delta S/R)$, where K is the intensity ratio I_{gauche}/I_{cis}, we obtained ΔH from the slope of the dependence of $-\ln K$ versus $1/T$. This conformer pair gave a ΔH value of 187 ± 20 cm^{-1} (2.24 ± 0.24 kJ/mol) with the *cis* conformer being the more stable form.

A portion of the infrared spectrum (1100–500 cm^{-1}) of 3-methyl-3-butene nitrile is shown in Fig. 2 and the bands observed at 570, 719, 805, 977 and 1025 cm^{-1} are assigned as fundamentals of the *gauche* conformer based on the predicted wavenumbers from the ab initio MP2/6-31G(d) calculation of 572, 718, 815, 970 and 1026 cm^{-1}, respectively. These predictions are remarkably good and in every case the corresponding *cis* mode is predicted with the correct relative value, i.e. the CH$_3$ rock is predicted at 1014 cm^{-1} for the *cis* mode (observed at 1014 cm^{-1}) whereas the CH$_3$ rock of the *gauche* conformer is predicted at 1026 cm^{-1}. None of these bands that are assigned as *gauche* modes are present in the solid which means the *cis* conformer is the more stable form in this phase.

The relative intensity of many of the *gauche* bands are stronger than the corresponding *cis* peaks but for most of these cases the predicted relative intensities are considerably larger. For example, the CH$_3$ rock at 1014 cm^{-1} for the *cis* form has a predicted intensity of 1.6 km/mol whereas the corresponding *gauche* mode has a predicted intensity of 8.6 km/mol. Similar differences are also predicted for the C=CC$_2$ deformations at 551 (*cis*) cm^{-1} with a predicted intensity of 0.9 km/mol whereas the *gauche* mode at 570 cm^{-1} has a predicted intensity of 2.8 km/mol. Therefore, the relative intensities of these bands cannot be conveniently used to predict the more stable conformer in the gas
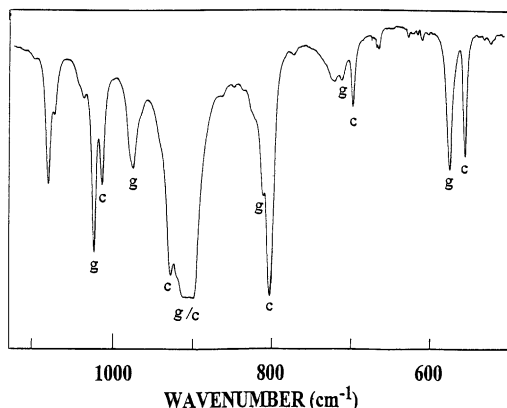

Fig. 2. Infrared spectrum (1100–500 cm^{-1}) of 3-methyl-3-butene nitrile in liquid xenon.

phase (xenon solution) without carrying out a temperature dependant study of the infrared spectrum.

In order to determine the enthalpy difference, ΔH, between the conformers of 3-methyl-3-butene nitrile, the relative intensities of the pair of bands at 551 (*cis*) and 570 (*gauche*) cm^{-1} were measured as a function of temperature from -55 to $-100°$C. The results are summarized in Table 1 and show that the intensities of the *cis* band increases, as the temperature is decreased compared to the intensities of the *gauche* band. Utilizing the van't Hoff equation, this conformer pair gives a ΔH value of 174 ± 20 cm^{-1} (2.08 $\pm$ 0.24 kJ/mol) with the *cis* conformer the more stable form. This value should be a reasonable estimate for the enthalpy difference in the gas phase as discussed elsewhere [3–7]. Since both of these molecules have an ethalpy difference considerably smaller than the value of 336 ± 61 cm^{-1} reported [2] for 3-buteneni-trile, it brings into question the correctness of this value. Therefore, the enthalpy value for 3-buteneni-trile should be determined again.

References

[1] G.H. Griffith, L.A. Harrah, J.W. Clark, J.R. Durig, J. Mol. Struct. 4 (1969) 255.

[2] J.R. Durig, G.A. Guirgis, A.S. Drew, J. Raman Spectrosc. 25 (1994) 907.

[3] W.A. Herrebout, B.J. van der Veken, J. Phys. Chem. 100 (1996) 9671.

[4] W.A. Herrebout, B.J. van der Veken, A. Wang, J.R. Durig, J. Phys. Chem. 99 (1995) 578.

[5] M.O. Bulanin, J. Mol. Struct. 347 (1995) 73.

[6] B.J. van der Veken, F.R. DeMunck, J. Chem. Phys. 97 (1992) 3060.

[7] M.O. Bulanin, J. Mol. Struct. 19 (1973) 59.

[8] C. Moller, M.S. Plesset, Phys. Rev. 46 (1934) 618.

[9] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98 (Revision A.7), Gaussian, Inc., Pittsburgh, PA, 1998.

[10] P. Pulay, Mol. Phys. 17 (1969) 197.