

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/242018578>

Infrared Spectra of Cyanoacetaldehyde (NCCH₂CHO): A Potential Prebiotic Compound of Astrochemical Interest

ARTICLE *in* CHEMPHYSCHEM · AUGUST 2013

Impact Factor: 3.42 · DOI: 10.1002/cphc.201300354 · Source: PubMed

CITATIONS

2

READS

46

5 AUTHORS, INCLUDING:



Abdessamad Benidar

Université de Rennes 1

42 PUBLICATIONS 275 CITATIONS

SEE PROFILE



Jean-claude Guillemin

Ecole Nationale Supérieure de Chimie de R...

385 PUBLICATIONS 3,367 CITATIONS

SEE PROFILE



Otilia Mó

Universidad Autónoma de Madrid

402 PUBLICATIONS 6,373 CITATIONS

SEE PROFILE



Manuel Yanez

Universidad Autónoma de Madrid

270 PUBLICATIONS 3,743 CITATIONS

SEE PROFILE

Infrared Spectra of Cyanoacetaldehyde (NCCH₂CHO): A Potential Prebiotic Compound of Astrochemical Interest

Abdessamad Benidar,^{*,[a]} Robert Georges,^[a] Jean-Claude Guillemin,^{*,[b]} Otilia Mó,^[c] and Manuel Yáñez^{*,[c]}

Cyanoacetaldehyde (NC–CH₂CH=O) and its isomer, cyanovinylalcohol (NC–CH=CH–OH), as possible components of the interstellar medium, comets, or planetary atmospheres, exist in equilibrium in the gas phase, although the latter compound is very much in the minority (2%). The recording and analysis of the gas-phase infrared spectrum of the former compound within the 4000–500 cm^{−1} spectroscopic range and the potential presence of the latter isomer, which could be vital for their detection in these media, are reported. CCSD(T) and G4 high-level ab initio methods, as well as density functional theory calculations, predict the existence of two stable rotamers of cyanoacetaldehyde. The global minimum has a structure with an

unusual O–C–C–C dihedral angle (150°) that falls between the antiperiplanar (180°) and anticlinal forms (120°). The second rotamer, which is about 4.0 kJ mol^{−1} less stable in terms of free energy, has a planar structure that corresponds to the synperiplanar form (O–C–C–C dihedral angle: 0°). The absorption vibrational bands of the two aldehyde rotamers that are present in the mixture lead to a spectrum with a very complex structure in the region of deformation movements, in which several low-intensity bands overlap. A complete and unambiguous assignment of the experimental spectrum has been achieved by using the calculated harmonic and anharmonic vibrational frequencies.

1. Introduction

Some compounds likely played a key role in the formation of larger molecules in the interstellar medium (ISM), comets, planetary atmospheres, or on the Primitive Earth, owing to their abundance in these media. Among such compounds, cyanoacetylene, which has already been detected in the atmosphere of Titan,^[1] in comets,^[2] in the ISM,^[3] and in simulations of the atmosphere of the Primitive Earth,^[4] has often been postulated as a probable and efficient starting material for the formation of more-complex compounds.^[5] Water, another abundant molecule in many places of the Universe, can add onto cyanoacetylene to give cyanoacetaldehyde and cyanovinylalcohol tautomers through Michael-type reactions and tautomeriza-

tion. However, water does not react easily with cyanoacetylene and the presence of a base is necessary to perform the reaction in the condensed phase. The addition reaction can occur in the gas phase but is endothermic.^[6]

Although it has never been detected in the ISM or comets, the role played by cyanoacetaldehyde on the Primitive Earth has often been proposed.^[5] Thus, in prebiotic conditions, the synthesis of cytosine or uracil, two pyrimidine bases, has been performed, starting from basic aqueous solutions of cyanoacetylene with urea, cyanate, or guanidine.^[7] In concentrated urea solution, cyanoacetaldehyde reacts to form cytosine in 30–50% yield, thus giving a plausible route to the pyrimidine bases that are required in the RNA world.^[8]

The synthesis of cyanoacetaldehyde under laboratory conditions is not easy and its characterization by using NMR spectroscopy was only achieved in 1991 by analysis of the pyrolysis products of a Meldrum's acid derivative.^[9] However, this approach, along with the others that have been reported in the literature,^[10] are not convenient for isolating a pure sample of this reactive compound. Cyanoacetaldehyde is kinetically less stable than the corresponding nitrogen and sulfur derivatives, for which the enamine^[11] and enethiol^[12] forms are kinetically more stable than the imine and thioaldehyde forms, respectively. However, some years ago, the flash vacuum pyrolysis of isoxazole with a low-temperature partial condensation of the gaseous flow allowed the first preparative synthesis and isolation of the cyanoacetaldehyde.^[13] Thanks to this approach, the microwave spectrum of cyanoacetaldehyde has been published very recently^[14] and the two keto conformers were observed in a comparable ratio to those that were predicted by

[a] Dr. A. Benidar, Prof. R. Georges
Institut de Physique de Rennes
CNRS UMR 6251
Université de Rennes 1
35042 Rennes (France)
E-mail: benidar@univ-rennes1.fr

[b] Dr. J.-C. Guillemin
Institut des Sciences Chimiques de Rennes
École Nationale Supérieure de Chimie de Rennes
CNRS, UMR 6226, Avenue du Général Leclerc
CS 50837, 35708 Rennes Cedex 7 (France)
E-mail: jean-claude.guillemin@ensc-rennes.fr

[c] Prof. O. Mó, Prof. M. Yáñez
Departamento de Química, Modulo 13
Universidad Autónoma de Madrid
Campus de Excelencia UAM-CSIC
Cantoblanco, 28049-Madrid (Spain)
E-mail: manuel.yanez@uam.es

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/cphc.201300354>.

ab initio theoretical calculations that were reported in the same study.^[14] However, attempts to detect the cyanovinylalcohol were unsuccessful. Herein, we report an experimental infrared spectroscopic study of cyanoacetaldehyde in the gas phase that complements the already-known spectroscopic MW information, which can be useful as far as the possible detection of these species in different media is concerned. The IR experimental information is complemented with density functional theory and high-level ab initio calculations, which have been shown to be useful in the unambiguous assignment of the vibration-rotation spectra of many species of astrochemical interest.^[15] In our case, these calculations were performed for the two rotamers of cyanoacetaldehyde and for all of the possible conformers of its isomer cyanovinylalcohol, which, in principle, can exist in equilibrium with the aldehyde, depending on the environmental conditions. The relative stability of the enol forms with respect to the aldehyde is a critical question as far as the correct assignment of their IR spectra is concerned and we pay particular attention to it. Hence, the main aim of this work is to provide new and relevant information on such compounds, which can help their detection in the ISM, comets, or the atmosphere of Titan.

Experimental Section

The synthesis of cyanoacetaldehyde was achieved in 24% yield by flash vacuum thermolysis at 770 °C under 0.1 mbar of isoxazole, a commercially available compound. The pure mixture of tautomers was obtained by a partial trapping of the gaseous flow at –28 °C; the expected product was trapped, whereas the much more volatile acetonitrile and the residual precursor were not. Infrared spectroscopic measurements of cyanoacetaldehyde in the gas phase at room temperature are very challenging, owing to the low vapor pressure of this compound at room temperature, at which vaporization and oligomerization compete. Vaporization of the sample at the lowest vaporization temperature to inhibit the decomposition was unsuccessful, but quick heating up to 50 °C gave better results. After a very short time at this temperature, to only afford the vaporization of a small part of the sample, the residual sample was quickly cooled in a liquid-nitrogen bath to stop the formation of unidentified dark-brown oligomeric products. This procedure can be repeated four or five times to allow the vaporization of about 20% of the starting material. The IR gas cell was maintained at a constant temperature of about 50 °C by using the circulation of a heating fluid through the double wall of the cell. The measured vapor pressure of the cyanoacetaldehyde/cyanovinylalcohol mixture was slightly lower than 0.1 mbar. The absorption cell was a stainless-steel tube (diameter: 33 cm, length: 220 cm) that was equipped with an optical White device.^[16] An adjustment of this multi-pass system to achieve a long optical path length of 136 m was required to compensate for the very low vapor pressure of the sample. The gas-phase IR spectrum was recorded on a 120HR Bruker Fourier-transform interferometer. A combination of a Globar source, a KBr beam splitter, and a liquid-nitrogen-cooled MCT detector was used to obtain the spectrum in the desired range (500–4000 cm^{–1}). Notably, the intensities of some of the characteristic bands of the studied compound diminished rather rapidly during the recording of the spectrum. Indeed, despite all of the precautions that were taken during the measurements, this compound began to decompose immediately after va-

porization and we noticed the formation of a brownish deposit in the cell at the end of the manipulations. Several successive fillings were necessary, which allowed us to record some twenty scans each time before significant decomposition of the sample occurred. The final spectrum was obtained by an average of 100 scans at a resolution of 0.5 cm^{–1} and is discussed below.

2. Computational Details

One critical point in the analysis of the spectra of molecules such as cyanoacetaldehyde is the possibility of several conformers (or even several isomers) existing in equilibrium. As a matter of fact, the relative proportion of the aldehyde and the alcohol strongly depends on the nature of the solvent used for the analysis in the condensed phase.^[9] Thus, a critical question is what is the relative proportion in the gas phase. Previous calculations in the literature predicted that the aldehyde was slightly more stable than the cyanovinylalcohol, but an accurate evaluation of the energy gap between both isomers is critical for making a reliable estimation of the actual proportions of both forms in the gas phase. For this reason, we decided to use CCSD(T) high-level ab initio calculations^[17] with different basis sets to calculate the structures and relative stability of the two conformers of cyanoacetaldehyde and the four conformers of its isomer, cyanovinylalcohol. For the sake of economy, the first survey was performed by using CCSD(T) calculations with geometries that were optimized at the B3LYP/6-31+G(d,p) level of theory and the 6-311+G(3df,2p) basis set (hereafter termed B1). However, to ensure that our calculations were converged, we also performed CCSD(T) calculations by using different Dunning's correlated consistent basis sets,^[18] the size of which increased in a systematic manner, namely B2=cc-pVTZ, B3=aug-pVTZ, and B4=aug-pVQZ. We also explored the effect of the quality of the geometries on the relative energies that were obtained by using B3LYP,^[19] M06,^[20] and CCSD approaches, together with a 6-311+G(d,p) basis-set expansion. Finally, we used high-level ab initio composite G4 theory, which provides total energies at an effective CCSD(T,full)/G3LargeXP+HF limit level.^[21] The G4 theory introduces several improvements over the previous levels of the *Gn* (*n*=1–3) suite of theories. With respect to G3, the main improvements include an evaluation of the HF limit to be added to the total energy calculation, the use of the CCSD(T) method to obtain the reference energy, in conjunction with larger basis sets than those used in the G3 approach,^[22] which contains a larger number of polarization functions, and the inclusion of two high-level empirical corrections. The geometry-optimization procedure and the calculation of the thermal corrections are also improved through the use of the B3LYP density functional theory (DFT) method with a 6-31G(2df,p) basis set. For the sake of completeness, we also investigated the performance of two very popular hybrid functionals, namely B3LYP^[19] and M06.^[20] With both functionals, the geometries were optimized by using the 6-311+G(d,p) basis sets, whereas the final energies were calculated in single-point calculations by using a 6-311+G(3df,2p) expansion if the func-

tional was B3LYP and an aug-cc-pVTZ basis set if the functional was M06.

The vibrational frequencies were obtained at both the B3LYP/6-311+G(3df,2p) and the M06/6-311+G(3df,2p) levels of theory, including anharmonicity corrections, through a numerical differentiation along the modes, as implemented in the Gaussian 09 series of programs,^[23] although the infrared intensities were calculated within the harmonic approximation.

3. Results and Discussion

In agreement with previous studies in the literature^[14] cyanoacetaldehyde has two stable rotamers, as shown in Figure 1.

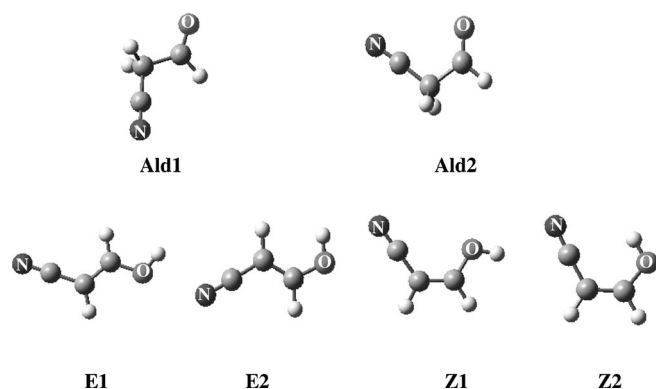


Figure 1. Stable conformers of cyanoacetaldehyde and cyanovinylalcohol.

The most-stable rotamer, **Ald1**, has a non-planar structure with a O-C-C-C dihedral angle of about 150° (147.9° at the B3LYP/6-31G(2df,p) level of theory). Notably, this result implies the existence of its enantiomeric form with an O-C-C-C angle of 212.1°. The second rotamer, **Ald2**, has a planar structure, which corresponds to the synperiplanar form (dihedral angle: 0°), and, therefore, has C_s symmetry. At the G4 level of theory, this rotamer is predicted to be 4.0 kJ mol⁻¹ less stable than **Ald1** in terms of their Gibbs free energies (Table 1). Moreover,

previous theoretical studies indicate that cyanovinylalcohol exists in four different conformations, two Z-type rotamers, namely **Z1** and **Z2**, and two E-type rotamers, namely **E1** and **E2**. All of these forms are planar structures with C_s symmetry and are less stable than both aldehyde rotamers. As shown in Table 1, **Z2**, which is stabilized by an OH...N intramolecular hydrogen bond, is the most-stable conformer, that is, 10.4 kJ mol⁻¹ higher in free energy than the global minimum, **Ald1**. The optimized geometries of all of these species are given in the Supporting Information, Table S1.

The harmonic and anharmonic vibrational frequencies for the three more-stable isomers at the B3LYP/6-311+G(3df,2p) level of theory, namely **Ald1**, **Ald2**, and **Z2** are summarized in Table 2 and Table 3, together with the calculated intensities and their corresponding assignments. The calculated values of the other three conformers of cyanovinylalcohol are summarized in Table S2. Notably, the values that were calculated with the M06 functional (Tables S3 and S4) did not differ significantly from the B3LYP ones; thus, in our discussion, only the B3LYP values are used.

As might be expected, the harmonic frequencies are consistently higher than the calculated ones if anharmonicity effects are taken into account. This correction is mainly important for the OH and CH stretching modes (spectroscopic region beyond 2500 cm⁻¹), in which the anharmonic/harmonic frequency ratio is of the order of 0.956. For the rest of the spectrum, the anharmonic correction provides a smaller change, which, on average, is 0.983.

The recorded experimental IR spectrum of the investigated equilibrium mixture is shown in Figure 2.

The analysis of this experimental spectrum is greatly facilitated by the data in Table 2 and Table 3, assuming that the **Ald1**, **Ald2**, and **Z2** species are all present in the gas phase. This analysis is particularly important within the spectroscopic region 600–1500 cm⁻¹, the structure of which is rather complex, owing to the presence of numerous low-intensity bands that often overlap. Bands assignment was possible thanks to spectroscopic deconvolution in this region by using the calculated values (Figure 3). Spectroscopic deconvolution was performed by using the self-deconvolution method introduced by Kauppinen et al. for resolving the overlapping peaks in spectroscopic regions in which the absorption is dense.^[24] In our spectrum, the bands were deconvoluted with a Lorentzian line-shape function and by using a resolution enhancement (line-narrowing) factor of 0.2 with a bandwidth of 30 cm⁻¹. This latter result is an estimate of the widths of the overlapping bands, whereas the enhancement is a measure of the resolving power that is applied to the data.

Table 1. Relative enthalpies and free energies (in parentheses) of the different conformers of cyanoacetaldehyde and cyanovinylalcohol at 298.2 K. All values are in kJ mol⁻¹.

Method ^[a,b]	Ald1	Ald2	E1	E2	Z1	Z2
B3LYP/B1	0 [0]	3.4 [5.4]	9.0 [13.0]	10.3 [13.8]	13.4 [16.7]	0.2 [4.4]
M06/B3	0 [0]	2.3 [4.3]	–	–	–	5.2 [9.3]
G4	0 [0]	2.5 [4.0]	16.6 [20.0]	18.1 [21.0]	20.3 [23.0]	6.9 [10.4]
CCSD(T)/B1	0 [0]	2.7 [4.7]	20.4 [24.5]	22.0 [25.4]	24.2 [27.6]	10.8 [14.9]
CCSD(T)/B2	0 [0]	2.7 [4.7]	–	–	–	7.8 [11.9]
CCSD(T)/B3/G1	0 [0]	2.7 [4.7]	17.3 [21.3]	–	–	7.3 [11.5]
CCSD(T)/B3/G2	0 [0]	–	–	–	–	7.9 [11.9]
CCSD(T)/B3/G3	0 [0]	2.6 [4.6]	–	–	–	7.3 [11.5]
CCSD(T)/B4/G1	0 [0]	–	–	–	–	5.4 [9.5]
CCSD(T)/B4/G2	0 [0]	–	–	–	–	5.5 [9.7]
CCSD(T)/B4/G3	0 [0]	–	–	–	–	5.4 [9.6]

[a] B1 = 6-311+G(3df,2p); B2 = cc-pVTZ; B3 = aug-cc-pVTZ; B4 = aug-cc-pVQZ. [b] G1, G2, and G3 stand for geometries that were optimized at the B3LYP/6-311+G(d,p), M06/6-311+G(d,p), and CCSD/6-311+G(d,p) levels of theory, respectively.

Table 2. Harmonic (ω) and anharmonic vibrational frequencies (ν) for the **Ald1** and **Ald2** rotamers of cyanoacetaldehyde, calculated at the B3LYP/6-311+G(3df,2p) level of theory. I_{IR} stands for the infrared intensities in km mole^{-1} .

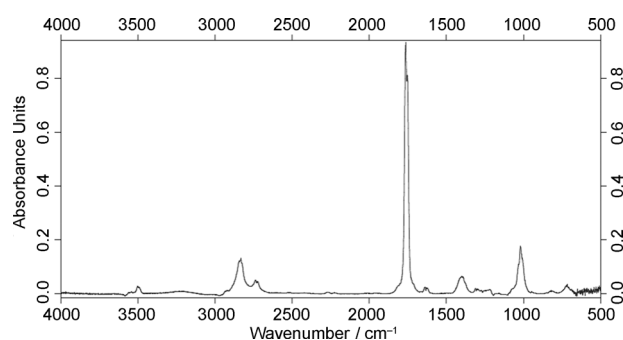
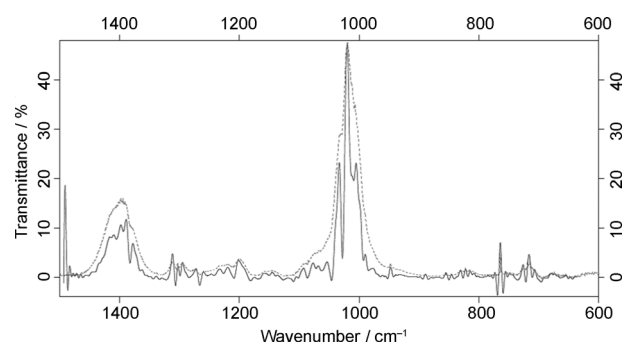
Assignment	Ald1			Ald2		
	ω [cm^{-1}]	I_{IR}	ν [cm^{-1}]	ω [cm^{-1}]	I_{IR}	ν [cm^{-1}]
OCH rocking	59	23.7	43	132	0.6	126
CCN+CCC bending	183	13.4	178	156	2.9	154
CCN bending (out of plane)	363	0.3	357	360	0.2	363
CCO+CCN bending	472	15.3	472	399	28.1	397
CCN+CCO bending (in plane)	526	1.3	520	732	5.0	717
CH ₂ rocking+CH bending (out of plane)	724	3.2	684	718	1.6	701
C–CN stretching	960	1.4	956	1001	12.5	986
CC stretching	1019	52.4	985	830	12.4	804
CH ₂ rocking+CH bending (out of plane)	1046	0.7	1030	1049	0.1	1030
CH ₂ twisting	1220	3.5	1200	1235	0.3	1208
CH ₂ wagging	1288	2.9	1259	1321	34.1	1288
CH bending (in plane)	1413	10.1	1417	1414	12.7	1428
CH ₂ scissoring	1437	11.4	1386	1438	17.8	1416
CO stretching	1825	221.4	1797	1835	155.1	1818
CN stretching	2359	9.0	2327	2370	4.7	2338
CH stretching	2925	52.8	2754	2898	97.2	2740
CH ₂ stretching (symmetric)	3023	3.4	2899	3022	7.7	2920
CH ₂ stretching (asymmetric)	3093	0.4	2949	3050	0.1	2909

tors. In general, there is good agreement between the experimental and calculated anharmonic frequencies. This agreement is also illustrated by comparing the simulated and observed spectra of this compound (Figure 4). The simulated spectrum was obtained by diverting anharmonic frequencies with Lorentz line shapes and a half width of 5 cm^{-1} and the intensities of each conformer were adjusted with respect to its estimated mole fraction. In spite of this overall agreement, there are some disturbing features in the experimental spectrum that do not match the theoretical predictions. In particular, the intensity of the OH stretching absorption, a single isolated band at

Table 3. Harmonic (ω) and anharmonic vibrational frequencies (ν) for the **Z2** conformer of cyanovinylalcohol, calculated at the B3LYP/6-311++(3df,2p) level of theory. I_{IR} stands for the infrared intensities in km mole^{-1} .

Assignment	Z2		
	ω [cm^{-1}]	I_{IR}	ν [cm^{-1}]
CCO bending (in plane)	138	9.2	138
CCN bending (out of plane)	301	6.9	299
CCN bending (in plane)	440	2.3	436
OH bending (out of plane)	531	46.4	517
OH bending (out of plane)	632	50.8	605
CH bending (out of plane)	735	42.6	725
CCC bending (in plane)	748	4.6	740
C–C stretching	959	7.7	943
CH bending (out of plane)	986	6.3	961
CH bending (in plane)	1112	90.2	1091
COH bending (in plane)	1241	135.0	1217
OH bending (in plane)	1369	6.3	1353
CH bending (in plane)	1426	6.6	1394
C=C stretching	1666	209.6	1623
CN stretching	2311	45.1	2277
CH stretching (asymmetric)	3198	3.8	3091
CH stretching (symmetric)	3216	1.6	3079
OH stretching	3737	48.7	3552

For this purpose, we assumed a Boltzmann-type distribution based on the free-energy gaps between these three isomers. By using this assumption and the G4 relative free energies that were calculated at 298.15 K, as well as the fact that there are two enantiomers for **Ald1**, the gas-phase mixture should contain 86% of **Ald1**, 12% of **Ald2**, and 2% of **Z2**. Notably, although this approach is reasonable under laboratory conditions, the interstellar medium is not a thermodynamic equilibrium environment and the proportion of the different conformers can be dictated by kinetic rather than thermodynamic fac-

**Figure 2.** IR spectrum of the equilibrium mixture that was obtained after re-vaporization (see the Experimental Section).**Figure 3.** IR spectrum of cyanoacetaldehyde within the 600–1400 cm^{-1} spectroscopic region. corresponds to the recorded spectrum; — corresponds to the deconvoluted spectrum.

3495 cm^{-1} , which is theoretically predicted to appear at 3552 cm^{-1} , is much larger than it should be for a relative amount of 2%. Although the other three enolic forms, **E1**, **E2**, and **Z1**, are expected to absorb in the same region (Table S2)

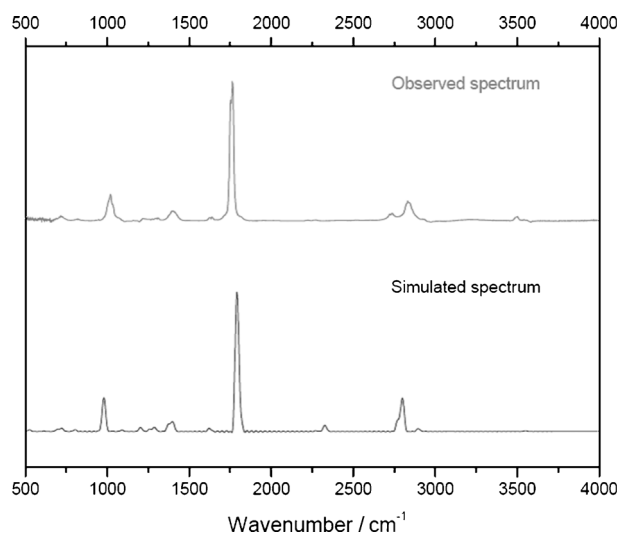


Figure 4. Comparison of the observed and simulated spectra of a mixture of cyanoacetaldehyde and cyanovinylalcohol. The simulated spectrum was obtained by convoluting the non-scaled anharmonic frequencies with Lorentz line shapes and a half-width of 5 cm^{-1} ; the intensities of each conformer were adjusted with respect to its estimated mole fraction.

with an oscillator strength that is two-times stronger for the **E1** form and four times stronger for both the **E2** and **Z1** forms, their very low stabilities clearly preclude their presence in the gas-phase equilibrium mixture. Hence, if one assumes that the **Z2** form is only present in a relative amount of 2%, one possible explanation for the intensity of the OH stretching band is a Fermi resonance between this band and combination bands, which absorb in the same region. Indeed, according to our anharmonic calculations, **Ald1** and **Ald2** show combination bands at 3525 and 3496 cm^{-1} , respectively.

Disappointingly, the previous dichotomy regarding the intensity of the OH absorption band cannot be resolved by considering the CH(OH) and CH(CN) vibrations. These modes are expected to absorb at 3091 and 3079 cm^{-1} with intensities of 1.6 and 3.8 kmol^{-1} , respectively. The correction of these intensities with the corresponding molar fraction of the enolic form (**Z2**) in the mixture renders these two modes so weak that they cannot be isolated from the spectroscopic noise. Another typical signature of the **Z2** isomer would be the C=C stretching mode, which is predicted to appear at 1623 cm^{-1} , in agreement with the observed experimental bands at 1630 cm^{-1} (Figure 2); however, this result is not conclusive either, because **Ald1** presents several combination bands (one at 1635 cm^{-1}) in this region of the spectrum.

4. Relative Stability and Abundance of the **Z2** Enolic Form

To solve the apparent dichotomy concerning the “real” proportion of the **Z2** isomer in the gas-phase equilibrium mixture, we decided to look in closer detail at this question, both from experimental and theoretical viewpoints.

We attempted to obtain some information on the isomeric composition by analysis of samples by low-temperature NMR

spectroscopy. Flash vacuum thermolysis was performed followed, on one hand, by direct condensation at 77 K of the gaseous flow and the addition of a NMR solvent or, on the other hand, by selective condensation at -28°C of cyanoacetaldehyde and cyanovinylalcohol before a partial flash distillation (quick heating of the trap at 50°C), condensation at 77 K , and the addition of an NMR solvent. Each sample was kept at low temperatures before analysis at -80°C and then at room temperature. Only the cyanoacetaldehyde was observed by using deuterated dichloromethane (CD_2Cl_2) as a solvent or, with the revaporized sample, by using deuterated toluene ($[\text{D}_8]\text{toluene}$). At room temperature, a 3:1 ratio of cyanoacetaldehyde to cyanovinylalcohol ($Z/E = 1:1$) was obtained with deuterated acetonitrile (CD_3CN) as a solvent. However, removing CD_3CN and adding $[\text{D}_8]\text{toluene}$ before NMR analysis (or the opposite) showed that the presence of the cyanovinylalcohol at room temperature was only dependent on the nature of the solvent. A similar conclusion was reached by Wentrup and co-workers,^[9] who found that, in the thermolysis of (alkylamino)methylene derivatives of Meldrum's acid, a mixture of cyanoacetaldehyde and cyanovinylalcohol was obtained, but the ratio of these two compounds was solvent dependent, as determined by ^1H NMR spectroscopy. However, we obtained a very interesting result by using deuterated acetone ($[(\text{CD}_3)_2\text{CO}]$) as a solvent. A revaporized sample that was diluted in $(\text{CD}_3)_2\text{CO}$, kept, and analyzed at -80°C only showed the presence of cyanoacetaldehyde. On heating at -40°C , trace amounts of the *Z*-cyanovinylalcohol were observed, whereas small amounts of the *Z* and *E* isomers were present at 0°C .

After several hours at room temperature, an equilibrium was observed with an *E/Z/Ald* ratio of $1:1.2:5.2$. In summary, revaporization of the thermolyzed products that are condensed at -28°C in vacuo only affords the cyanoacetaldehyde.

From a theoretical point of view, we calculated the stability of the **Z2** form with respect to the **Ald1** rotamer by using different theoretical models, the outcomes of which are given in Table 1. With the only exception of the B3LYP DFT approach, all of the other theoretical schemes (including the M06 DFT approach) predict that the proportion of the **Z2** form is always less than 2.5%. Notably, by comparing the last six rows in Table 1, these estimations are independent of the method that is used for the geometry optimization. There are some slight differences on changing from the 6-311+G(3df,2p) basis set to the cc-pVTZ basis set (3 kJ mol^{-1}), but no significant changes are observed on including diffuse components in the latter set. Enlarging the basis set from TZ to QZ leads to a slight decrease in the energy gap between the **Z2** and **Ald1** species of about 2 kJ mol^{-1} , but the obtained values differ by less than 1 kJ mol^{-1} from those calculated at the G4 level of theory and, therefore, our high-level ab initio calculation can be considered as converged. Hence, we must conclude that the proportion of **Z2** in the gas-phase mixture should not exceed 2.5%.

On the other hand, our B3LYP/6-311+G(d,p) calculations are consistent with the experimental finding discussed above that, at low temperatures, the mixture only contains cyanoacetaldehyde, because the **TS1** transition state, which connects the **Ald1** and **Z2** structures, is extremely high (245 kJ mol^{-1}), thus

excluding any possibility of observing such a tautomerization in the gas phase under the conditions used in our experiments.

We also explored the possibility that this tautomerization can proceed through a double proton transfer from (**Ald1**)₂ dimers to (**Z2**)₂ dimers. Indeed, **Ald1** forms weakly bound dimers that are stabilized by CH...O intermolecular hydrogen bonds (Figure 5). These (**Ald1**)₂ dimers are predicted to be 14 kJ mol⁻¹ lower in enthalpy than the monomers at the G4 level of theory. However, although the barrier for the double

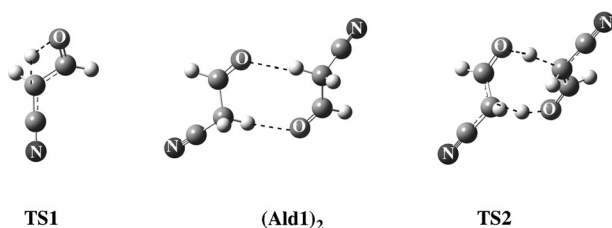


Figure 5. Structures of transition state **TS1**, which connects structures **Ald1** and **Z2**, the **Ald1** dimer, and the transition state that connects structures (**Ald1**)₂ and (**Z2**)₂ through a double proton transfer.

proton transfer within the dimer through transition state **TS2** (Figure 5) is much lower (161 kJ mol⁻¹) than that associated with the tautomerization of the monomer, it is still too high to allow for a conversion of (**Ald1**)₂ into (**Z2**)₂ under the actual experimental conditions.

In summary, our detailed exploration on both experimental and theoretical grounds is consistent with a very small presence of the enol form, but perhaps the metallic nature of the walls of the IR cell that is used in the experiments may favor the formation of a certain amount of the alcohol, which would explain the presence of the OH band in the spectra.

5. Spectroscopic Analysis

In what follows, we try to identify the main absorption bands in the spectra that are associated with the two aldehyde rotamers. As was the case for the CH(OH) and CH(CN) vibrations discussed above, the antisymmetric CH₂ stretching mode, which is expected to be observed at 2949 cm⁻¹ for **Ald1** and at 2909 cm⁻¹ for **Ald2**, has a very low intensity that does not allow for their assignment in the experimental spectrum. The symmetric CH₂ stretching and the CH stretching modes of the aldehyde components in the mixture absorb within a narrow spectroscopic range so that their bands overlap, thus leading to a poorly resolved absorption profile that is centered at 2840 cm⁻¹. Finer analysis of this region allowed us to assign the observed values at 2926 and 2831 cm⁻¹ for the most-stable aldehyde to CH₂ symmetric stretching and CH stretching vibrations, respectively. These values are in rather good agreement with the calculated ones (2899 and 2754 cm⁻¹). For **Ald2**, these two vibrational modes absorb at 2882 and 2730 cm⁻¹, again in good agreement with the calculated frequencies (2920 and 2740 cm⁻¹). We assigned the observed band at

2265 cm⁻¹ to the CN stretch, which was predicted to appear at 2327 and 2338 cm⁻¹ for **Ald1** and **Ald2**, respectively. The difference between the calculated and observed values is larger than for other modes, but, as shown previously by Botschwina et al.,^[15a,25] an adequate description of the CN bond length and the corresponding stretching frequency can only be achieved if high-level CCSD(T) calculations that are associated with large basis sets are used. A good alternative for obtaining more-accurate values for the vibrational frequencies of these modes is the use of a hybrid force field, as proposed by Pouchan and co-workers.^[26] Disappointingly, such levels of calculation are too computationally demanding for systems of the size of cyanoacetaldehyde, owing to its low symmetry. However, we performed calculations of the CN stretching frequencies for the three forms, **Ald1**, **Ald2**, and **Z2**, at the CCSD/6-311+G(d,p) level of theory and, although the calculated values are about 1% smaller than those reported above, they are still too large with respect to the experimental values, thus indicating that triple substitutions are required to have a more-quantitative agreement. Because the oscillator strength of this stretching is predicted to be five-times greater in the **Z2** enol than in **Ald1** and ten times greater than in **Ald2**, in spite of the low proportion of the **Z2** form in the mixture, a weak band is observed at 2224 cm⁻¹, which should be assigned to the CN vibration (predicted at 2277 cm⁻¹). The CO vibration in both rotameric aldehydes is the most-intense absorption band of the experimental spectrum. We used this isolated characteristic band of aldehydes to validate our calculations of the relative stability of the two rotamers and, thus, their relative concentrations in the mixture at room temperature. Indeed, the intensities of the CO band in both cyanoacetaldehyde rotamers, as determined from harmonic calculations, are in a ratio of 1.4:1 in favor of the more-stable aldehyde. In the observed spectrum, the ratio is ten-times larger, but this difference between the measured and calculated ratios disappears if using the intensities that are weighted with the mole fraction of each of the rotamers. We attribute the CO vibration to the 1802 and 1759 cm⁻¹ bands of **Ald1** and **Ald2**, respectively, in perfect agreement with the theoretical predictions; the vibrations that correspond to deformation of the CH₂ group in both aldehydes, namely CH₂ scissoring, CH₂ wagging, CH₂ twisting, and CH₂ rocking, are predicted to be of moderate-to-low intensity. Coherently, in the experimental spectrum of the mixture, these deformation bands appear as weak to very weak bands. We found a very good agreement with the calculated frequencies for the CH₂ scissoring modes, which were predicted to be at 1400 and 1395 cm⁻¹ and observed at 1416 and 1386 cm⁻¹ for the two forms of the cyanoacetaldehyde. The CH₂ wagging vibration is expected to have an oscillator strength that is 10-times greater in **Ald2** than in **Ald1**. After the correction that accounts for the relative stability of two rotamers, this vibration must have approximately the same magnitude for both aldehydes and absorb at the same frequency (1266 cm⁻¹). The experimental value of the CH₂ twisting mode was assigned to the 1215 cm⁻¹ band (calculated at 1200 cm⁻¹ for **Ald1**). However, the same mode of **Ald2** (calculated to 1208 cm⁻¹) was very difficult to identify in the experimental spectrum. The CH₂ rocking mode appears

coupled to the out-of-plane CH bending. This vibration, which is predicted to absorb at 1030 cm^{-1} for **Ald2**, is extremely weak and, hence, it is not detected in our spectrum. Conversely, the weak band at 1030 cm^{-1} was attributed to the same mode for **Ald1**, in agreement with the calculated value at 1030 cm^{-1} . There is another band that is associated with coupling between the CH_2 rocking and the out-of-plane CH bending, which are expected to be found at lower frequencies, that is, 684 cm^{-1} for **Ald1** and 701 cm^{-1} for **Ald2** and are experimentally observed at 676 cm^{-1} and 707 cm^{-1} , respectively. The CH deformation mode in the two aldehyde rotamers is expected to be insensitive to the rotameric effect and must absorb at almost the same frequency in both aldehydes. This vibrational mode should correspond to the absorption band at 1380 cm^{-1} , in good agreement with the corresponding anharmonic calculated values, 1417 and 1428 cm^{-1} . The signatures of the CC vibration in aldehyde compounds are located at around 900 cm^{-1} . One can distinguish those that belong to the central CC stretching from those that belong to the C–CN stretch, but there is a significant difference between both rotamers in what respect the frequencies of these two stretching modes. Whereas for **Ald1**, the central CC stretching appears at higher frequency (985 cm^{-1}) than the C–CN stretching mode (956 cm^{-1}) and it is significantly more intense, for **Ald2**, the C–CN stretching is the one that is observed at higher frequency (986 cm^{-1} vs 804 cm^{-1}) and both absorptions have similar intensity.

There are also five additional bands outside the frequency range that is covered in our experiments, that is, vibrational modes that absorb below 600 cm^{-1} . The most-significant ones are associated with in-plane and out-of-plane CCN bending modes, which appear coupled with CCO bending displacements. The different relative orientation of the CN group with respect to the CO group results in significant differences between the frequencies of these bands for **Ald1** and **Ald2** (472 vs 397 cm^{-1} and 520 vs 717 cm^{-1}). The lowest-frequency vibration corresponds to an OCH rocking mode. Here again, there are some inversions between **Ald1** and **Ald2** as far as the frequencies are concerned. For the former rotamer, the in-plane CCN bending appears at a higher frequency (520 cm^{-1}) than the CCO bending (472 cm^{-1}), whereas, for rotamer **Ald2**, the frequencies are the other way around, that is, the CCO bending is observed at 717 cm^{-1} and the CCN one appears at 397 cm^{-1} .

6. Concluding Remarks

One of the critical points regarding the spectroscopic behavior of cyanoacetaldehyde ($\text{NC}-\text{CH}_2\text{CH}=\text{O}$) is the number of the possible rotamers of the aldehyde and the potential presence of some of the four conformers of its isomer, cyanovinylalcohol. A careful investigation of this point from both the theoretical and experimental viewpoints agree that, in the gas-phase equilibrium mixture, the amount of the enolic **Z2** structure is never larger than 2.5%. Hence, the equilibrium mixture contains essentially the two aldehyde rotamers, with **Ald1** clearly dominant. Also taking into account that no aldehyde/alcohol isomerization should be expected under the experimental con-

ditions, the rather small amount of the vinyl alcohol as detected by the OH band at 3495 cm^{-1} could perhaps originate from the walls of the cell. The absorption vibrational bands of the two aldehyde rotamers present in the mixture lead to a spectrum with a very complex structure in the region of deformation movements, in which several low-intensity bands overlap. A complete and unambiguous assignment of the experimental spectrum has been achieved by using the calculated harmonic and anharmonic vibrational frequencies.

Acknowledgements

This work was supported by the Dirección General de Investigación (DGI) (CTQ2012-35513-C02-01 and CTQ2010-17006), by the MADRISOLAR2 Project of the Comunidad Autónoma de Madrid (S2009PPQ/1533), and by the Consolider on Molecular Nanoscience (CSC2007-00010). Generous allocation of computation time at the Centro de Computación Científica (CCC) of the Universidad Autónoma de Madrid (UAM) is also acknowledged. J.-C. G. and A.B. thank the Programme National de Physique et Chimie du Milieu Interstellaire (PCMI) and the Centre National d'Etudes Spatiales (CNES) for financial support.

Keywords: ab initio calculations • astrochemistry • cyanoacetaldehyde • density functional calculations • IR spectroscopy

- [1] A. Coustenis, B. Schmitt, R. K. Khanna, F. Trotta, *Planet. Space Sci.* **1999**, 47, 1305–1329.
- [2] D. Bockelee-Morvan, D. C. Lis, J. E. Wink, D. Despois, J. Crovisier, R. Bachiller, D. J. Benford, N. Biver, P. Colom, J. K. Davies, E. Gerard, B. Germain, M. Houde, D. Mehringer, R. Moreno, G. Paubert, T. G. Phillips, H. Rauer, *Astron. Astrophys.* **2000**, 353, 1101–1114.
- [3] J. E. Dickens, W. M. Irvine, A. Nummelin, H. Møllendal, S. Saito, S. Thorwirth, Å. Hjalmarson, M. Ohishi, *Spectrochim. Acta Part A* **2001**, 57, 643–660.
- [4] G. Toupance, F. Raulin, R. Buvet, *Origins Life* **1975**, 6, 83–90.
- [5] L. E. Orgel, *Origins Life Evol. Biosphere* **2002**, 32, 279–281.
- [6] A. Horn, H. Møllendal, J. C. Guillemin, *J. Phys. Chem. A* **2008**, 112, 11009–11016.
- [7] a) S. L. Miller, *J. Am. Chem. Soc.* **1955**, 77, 2351–2361; b) R. Lohrmann, *J. Mol. Evol.* **1972**, 1, 263; c) J. P. Ferris, O. S. Zamek, A. M. Altbuch, H. Freeman, *J. Mol. Evol.* **1974**, 3, 301–309.
- [8] a) M. P. Robertson, S. L. Miller, *Nature* **1995**, 377, 257–257; b) M. P. Robertson, S. L. Miller, *Nature* **1995**, 375, 772–774.
- [9] A. Ben Cheikh, J. Chuche, N. Manisse, J. C. Pommélet, K. P. Netsch, P. Lorencak, C. Wentrup, *J. Org. Chem.* **1991**, 56, 970–975.
- [10] V. A. dos Santos, L. S. Shul'pina, D. Veghini, D. Mandelli, G. B. Shul'pin, *React. Kinet. Catal. Lett.* **2006**, 88, 339–348.
- [11] A. Benidar, J.-C. Guillemin, O. Mó, M. Yáñez, *J. Phys. Chem. A* **2005**, 109, 4705–4712.
- [12] A. Benidar, R. Georges, J. C. Guillemin, O. Mó, M. Yáñez, *J. Phys. Chem. A* **2010**, 114, 9583–9588.
- [13] A. Luna, O. Mó, M. Yáñez, J. C. Guillemin, J. F. Gal, P. C. Maria, *Int. J. Mass Spectrom.* **2007**, 267, 125–133.
- [14] H. Møllendal, L. Margules, R. A. Motiyenko, N. W. Larsen, J. C. Guillemin, *J. Phys. Chem. A* **2012**, 116, 4047–4056.
- [15] a) P. Botschwina, R. Oswald, *Chem. Phys. Lett.* **2000**, 319, 587–594; b) R. K. Khanna, M. S. Lowenthal, H. L. Ammon, M. H. Moore, *Astrophys. J. Suppl. Ser.* **2002**, 140, 457–464; c) M. L. Senent, M. Villa, F. J. Melendez, R. Dominguez-Gomez, *Astrophys. J.* **2005**, 627, 567–576; d) M. L. Senent, H. Masso, M. Hochlaf, *Astrophys. J.* **2007**, 670, 1510–1517; e) V. Špirko, O. Bludský, W. P. Kraemer, *Collect. Czech. Chem. Commun.* **2008**,

- 73, 873–897; f) N. Inostroza, J. R. Letelier, M. L. Senent, P. Fuentealba, *Spectrochim. Acta Part A* **2008**, *71*, 798–802; g) D. Ben Abdallah, K. Hammami, F. Najar, N. Jaidane, Z. B. Lakhdar, M. L. Senent, G. Chambaud, M. Hochlaf, *Astrophys. J.* **2008**, *686*, 379–383; h) T. Pasinszki, M. Krebsz, G. Bazso, G. Tarczay, *Chem. Eur. J.* **2009**, *15*, 6100–6102; i) M. Hochlaf, G. Chambaud, M. L. Senent, *Mol. Phys.* **2010**, *108*, 1277–1284; j) M. L. Senent, *J. Math. Chem.* **2011**, *49*, 1424–1435; k) D. Bégué, N. Gohaud, C. Pouchan, P. Cassam-Chenaie, J. Liévin, *J. Chem. Phys.* **2007**, *127*, 164115; l) P. Carbonniere, C. Pouchan, *Theor. Chem. Acc.* **2012**, *131*, 1183.
- [16] J. U. White, *J. Opt. Soc. Am.* **1942**, *32*, 285–288.
- [17] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Headgordon, *Chem. Phys. Lett.* **1989**, *157*, 479–483.
- [18] D. E. Woon, T. H. Dunning, *J. Chem. Phys.* **1993**, *98*, 1358–1371.
- [19] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [20] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [21] L. A. Curtiss, P. C. Redfern, K. Raghavachari, *J. Chem. Phys.* **2007**, *126*, 084108.
- [22] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, J. A. Pople, *J. Chem. Phys.* **1998**, *109*, 7764–7776.
- [23] Gaussian 09 (Revision A.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
- [24] J. K. Kauppinen, D. J. Moffatt, H. H. Mantsch, D. G. Cameron, *Appl. Spectrosc.* **1981**, *35*, 271–276.
- [25] a) P. Botschwina, A. Heyl, M. Oswald, T. Hirano, *Spectrochim. Acta Part A* **1997**, *53*, 1079–1090; b) A. Huckauf, A. Guarnieri, A. Heyl, P. Botschwina, C. Bartel, D. Lentz, *Chem. Phys. Lett.* **1999**, *303*, 607–615; c) L. Biz-zocchi, C. D. Esposti, P. Botschwina, *J. Mol. Spectrosc.* **2004**, *225*, 145–151; d) R. Kołos, M. Gronowski, P. Botschwina, *J. Chem. Phys.* **2008**, *128*, 154305; e) P. Botschwina, R. Oswald, *J. Mol. Spectrosc.* **2009**, *254*, 47–52.
- [26] D. Begue, P. Carbonniere, C. Pouchan, *J. Phys. Chem. A* **2005**, *109*, 4611–4616.

Received: April 9, 2013

Published online on June 24, 2013