Conformational study of 1,2-diaminoethane by combined ab initio MO calculations and Raman spectroscopy

L.A.E. Batista de Carvalho*, L.E. Lourenço, M.P.M Marques

Unidade I&D Química-Física Molecular, Fac. Ciências e Tecnologia, Universidade de Coimbra, P-3049 Coimbra, Portugal

Abstract

A conformational analysis of the linear polyamine 1,2-diaminoethane was performed by both Raman spectroscopy and ab initio SCF-MO methods (with and without inclusion of water solvent effects). Ten different conformers were detected by ab initio calculations, the most stable ones being TGG′ and GGG′. When considering the solvent, the conformations having a higher dipole moment were found to be favoured over the less polar ones. The Raman spectra of this amine obtained for the pure liquid, the aqueous solution and the solid sample, allowed to conclude that its conformational preferences are determined by the relative importance of intra- versus intermolecular hydrogen bonds. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: 1,2-Diaminoethane; Conformational analysis; Raman spectroscopy; Ab initio MO

1. Introduction

1,2-diaminoethane ($H_2N(CH_2)_2NH_2$) and the larger similar molecules 1,3-diaminopropane and 1,4-diaminobutane (putrescine) are widely used as chelating agents for some metal ions, and are precursors of biologically relevant polyamines (e.g. spermidine and spermine) that play an essential role in cell growth and differentiation in eukaryotic organisms. Moreover, some metal complexes (e.g. Pt^{2+}) formed with these amines are known to display anticancer properties through DNA-binding. However, the exact nature of the biochemical mechanisms through which they act is still unknown, and has been the topic of intense research in recent years.

Rotational isomerism in alkylamines is influenced by different factors, from steric, dipolar and hyperconjugative effects to hydrogen bonding. Moreover, the relative importance of intra versus intermolecular interactions has proved to be determinant of the conformational preferences of this kind of systems, either as pure compounds or in solution [1–7].

Several conformational studies have been reported in the literature for 1,2-diaminoethane, the simplest linear polyamine. While it adopts an all-*trans* geometry in the solid state [8,9], it was shown – by electron diffraction and microwave methods [10,11] – to display rotational isomerism in the gaseous state, the predominant species being the *gauche* conformers relative to the central C–C bond. In the liquid phase, in turn, no conclusive answers have yet been obtained to explain the conformational behaviour of this diamine.

The analysis of the FTIR and Raman spectra of this molecule and its deuterated derivatives led to the detection of distinct conformations in the pure liquid [12–15]. These results have been interpreted in terms

---

* Corresponding author. Tel.: + 351 39 826541; fax: + 351 39 826541.

E-mail address: labc@gemini.ci.uc.pt (L.A.E. Batista de Carvalho)

Table 1
Ab initio relative energies, populations and dipole moments (μ) calculated for the distinct conformers of 1,2-diaminoethane

Conformer (symmetry)	μ^a (D)	ΔE/kJ mol^{-1}(population, %)[b]		SCRF[c]	SCRF
		3-21G(N*)	MP2/6-31G**	3-21G(N*)	MP2/6-31G**
TGG' (C$_1$)	2.98	0 (52.5)	0 (41.0)	0 (63.4)	0 (69.4)
GGG' (C$_1$)	2.40	1.62 (27.3)	0.73 (30.5)	2.19 (26.2)	3.13 (19.6)
TGG (C$_1$)	2.77	8.27 (1.9)	5.93 (3.8)	7.33 (3.3)	7.35 (3.6)
GGG (C$_2$)	0.31	5.99 (4.7)	2.71 (13.8)	10.72 (0.8)	7.83 (3.0)
TTG (C$_1$)	2.77	6.94 (3.2)	7.77 (1.8)	7.24 (3.4)	8.80 (2.0)
GG'G (C$_2$)	1.95	20.07 (0)	17.38 (0)	21.64 (0)	20.48 (0)
TTT (C$_{2h}$)	0	5.32 (3.1)	5.35 (2.4)	10.17 (0.5)	10.52 (0.5)
TGT (C$_2$)	0.45	8.11 (2.0)	5.48 (4.5)	12.92 (0.4)	10.56 (1.0)
GTG (C$_2$)	2.32	7.82 (2.2)	9.30 (1.0)	9.32 (1.5)	11.33 (0.7)
GTG' (C$_i$)	0	6.99 (3.1)	8.66 (1.2)	11.83 (0.5)	13.84 (0.2)

[a] Calculated at the SCRF (water) //MP2/6-31G** level (1 D $=$ 1/3 $\times$ 10^{-2} C m).
[b] Calculated at 25°C.
[c] In Water, $\epsilon^{25°C} =$ 78.54.

of the rotation around the central C–C bond, but no reference has been made as to the orientation of the nitrogen electron lone-pairs.

Previously performed ab initio MO calculations found ten different energy minima for this molecule [16–19]. Nevertheless, no attempts have been made either to mimetize aqueous solution conditions or to obtain the calculated vibrational spectra of the distinct conformers. Also, there are no reports on a normal coordinate analysis performed for this system.

In the present work, 1,2-diaminoethane was studied by both Raman spectroscopy and ab initio MO calculations. A conformational analysis was performed, based on the vibrational data and the theoretical calculations – geometries, wavenumbers and intensities – for both the isolated molecule and considering a solvent (water) reaction field, in order to understand the conformational changes caused by the presence of the solvent and the factors that govern them. A complete assignment of the vibrational spectra was made, for both the non-deuterated and N-deuterated molecules. A normal coordinate analysis was carried out, using local symmetry coordinates and the calculated ab initio force field.

2. Experimental

The ab initio SCF-MO calculations were carried out as previously reported [20], using the GAUSSIAN 94 program [21], with the split valence basis sets 3-21G(N*), 6-31G** and MP2/6-31G** [22–28]. Only the geometries with skeletal dihedral angles equal to 60°, 180° and −60° were considered for the conformational search. The presence of the solvent (water) was simulated by performing Self-Consistent Reaction Field (SCRF) ab initio MO calculations [29]. The normal coordinate analysis of the molecule was undertaken using the GF Wilson's method.

Raman spectra were recorded on a Spex 1403 Ramalog double spectrometer, as published earlier [7]. The light source was a Spectra Physics Ar$^+$ laser whose output at 514.5 nm was adjusted to provide 100 mW at the sample position.

1,2–diaminoethane (redistilled, 99.5 $+$ %) was obtained from Aldrich and used without further purification. 1,2-diaminoethane-N-d$_4$ was prepared by repeatedly stirring a 1 : 1 mixture of the pure compound and D$_2$O for ca. 1 h, followed by distillation.

3. Results and discussion

3.1. Ab initio MO results

Ten distinct minima were found for 1,2-diaminoethane (Table 1, Fig. 1). The most populated
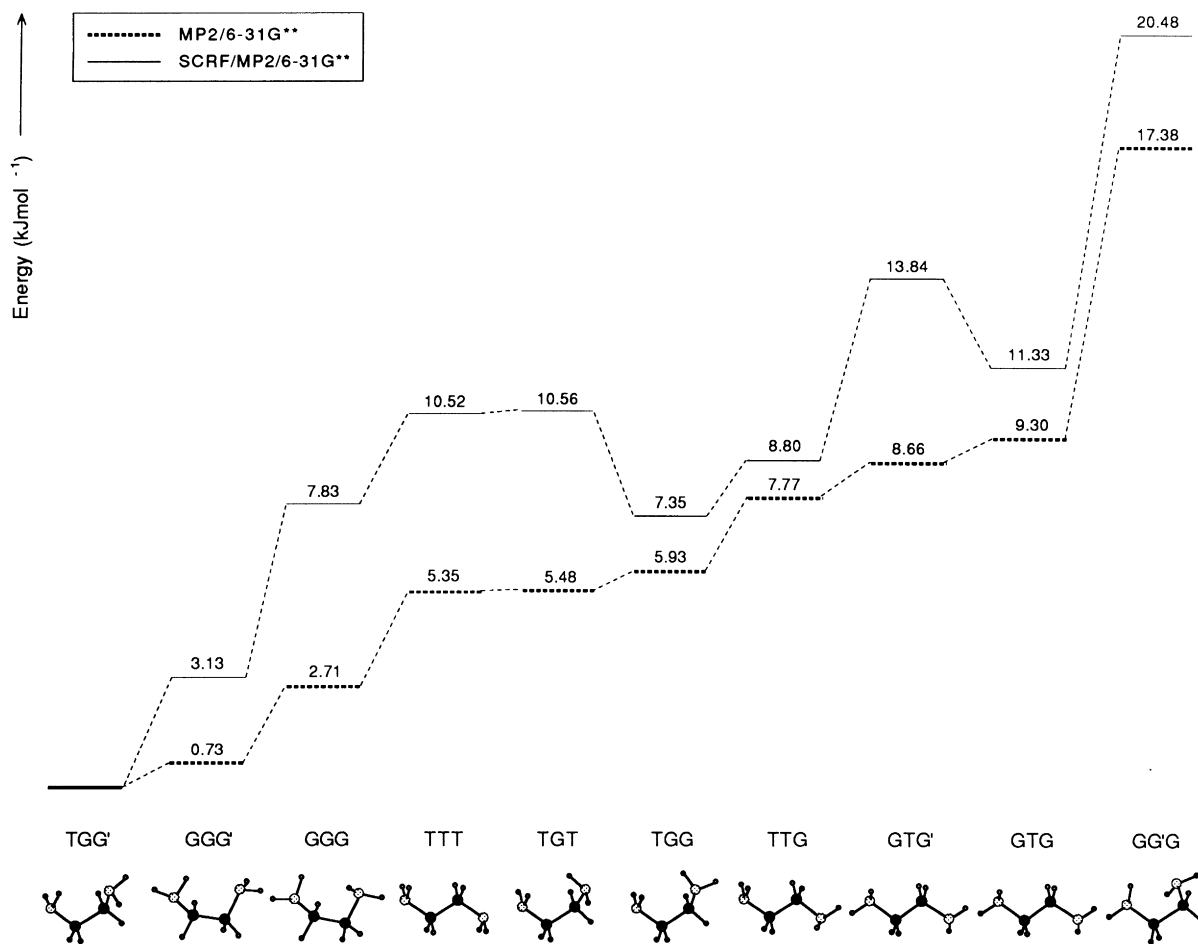
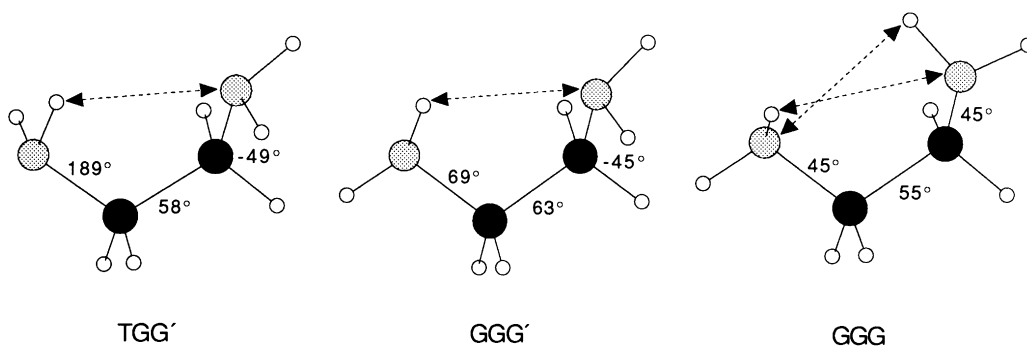Fig. 1. Schematic representation of the conformational energies calculated for 1,2-diaminoethane.

Fig. 2. Schematic representation of the most stable conformers of 1,2-diaminoethane, displaying intramolecular (N)H⋯:N interactions.
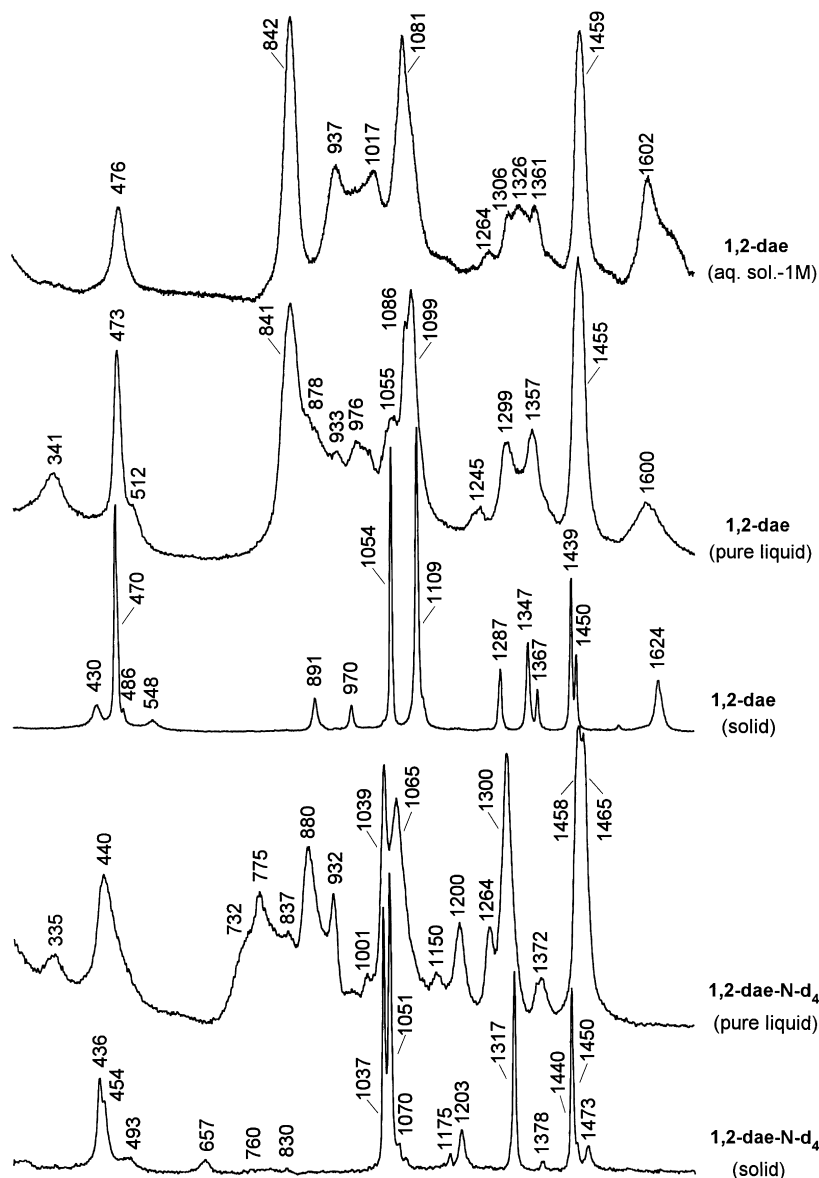
Fig. 3. Raman spectra (250–1700 cm^{-1}) of 1,2-diaminoethane (1,2-dae) and 1,2-diaminoethane-N-d$_4$ (1,2-dae-N-d$_4$) in aqueous solution (1 M), pure liquid (293 K) and solid phase.

conformers – TGG′ and GGG′ – display *gauche* skeletal orientations, that allow the occurrence of stabilising intramolecular (N)H···:N hydrogen bonds (Fig. 2). The presence of this kind of interaction is confirmed by both the calculated geometrical parameters (available from the authors upon request) – namely the NCCN and :NCC dihedral angles

(Fig. 2) and the CNH bond angles – and the changes detected in the Mulliken charges of the atoms involved.

It was verified that the smaller basis set 3-21G(N*) reproduces rather well the energies of the *trans* conformations relative to the central C–C bond. However, inclusion of electron correlation effects

Table 2
Raman experimental and calculated wavenumbers (cm^{-1}) for some conformers of 1,2-diaminoethane (1,2-dae) and 1,2-diaminoethane-N-d$_4$ (1,2-dae-N-d$_4$)

Experimental					Calculated[a]			Approximate descriptions and PED (%) values[b]
1,2-dae Aq. Sol.	Liquid	Solid	1,2-dae-N-d$_4$ Liquid	Solid	1,2-dae TGG$'$	GGG$'$	TTT	
3370	3360	3335			3444 3425	3447	3436 Bg	NH$_2$ antisym. stretching (100)
		3252						
3310	3300	3169			3347 3333	3349	3340 Ag	NH$_2$ sym. stretching (100)
	3190							FR[c] (2 × NH$_2$ sciss. + NH$_2$ sym. str.)
					2981	2990		
2942	2917	2909	2933	2930	2958	2959	2962 Bg	CH$_2$ antisym. stretching (100)
		2897		2893				FR[c] (2 × CH$_2$ sciss. + CH$_2$ sym. str.)
2880	2858	2856	2872	2868	2919 2867	2883 2841	2915 Ag	CH$_2$ sym. stretching (100)
			2513	2504				ND$_2$ antisym. stretching
			2434	2429				ND$_2$ sym. stretching
			2371	2367				ND$_2$ sym. stretching
1602	1600	1624			1602 1589	1588 1577	1594 Ag	NH$_2$ scissoring (100)
			1465	1473	1463	1473		CH$_2$ scissoring
1459	1455	1450	1458	1450	1447	1457	1441 Ag	CH$_2$ scissoring (100)
		1439		1440				CH$_2$ scissoring
1361	1357	1367	1372	1378	1343	1353	1352 Ag	CH$_2$ wagging (100)
1326		1347			1336	1293	1319 Ag	CH$_2$ twisting (55) + NH$_2$ twisting (25)
1306	1299				1272	1277		CH$_2$ twisting + NH$_2$ twisting
			1300	1317				CH$_2$ wagging
1264	1245	1287					1257 Bg	NH$_2$ twisting (31) + CH$_2$ twisting (30)
			1264					CH$_2$ twisting
			1200	1203				ND$_2$ deformation
			1150	1175				
1081	1099	1109	1065	1051			1086 Ag	CN stretching (58)
	1086				1069	1086		CN stretching
		1055	1054	1039	1037		1039 Ag	CH$_2$–CH$_2$ stretching (67)
			1001	1070				ND$_2$ twisting
	976		932		970	1024		CN stretching
937	933	970					906 Bg	CH$_2$ rocking (55) + ND$_2$ twisting (45)
			880					CN stretching
	878				884	873		NH$_2$ wagging + CH$_2$–CH$_2$ stretching
842	841	891			792	804	829 Ag	NH$_2$ wagging (80) + CN stretching (20)
			775	830				CH$_2$ rocking
			732	760				ND$_2$ wagging
				657				
		548						(470 + 88 cm^{-1}) combination mode

Table 2 (*continued*)

Experimental					Calculated[a]			Approximate descriptions and PED (%) values[b]
1,2-dae Aq. Sol.	Liquid	Solid	1,2-dae-N-d$_4$ Liquid	Solid	1,2-dae TGG'	GGG'	TTT	
	512				528	521		CCN deformation
				493				(436 + 79 cm^{-1}) combination mode
		486		454				CCN deformation
476	473	470	440	436			472 Ag	CCN deformation (48)
		430					324 Bg	NH$_2$ torsion (98)
	341		335		366	368		CCN deformation + NH$_2$ torsion
				280				ND$_2$ torsion
	190			220	196	201		CH$_2$–CH$_2$ torsion
		177		182				Lattice vibrations
		150		143				Lattice vibrations
		129		108				Lattice vibrations
		102		99				Lattice vibrations
		88		79				Lattice vibrations

[a] MP2/6-31G**level; scaled by a factor of 0.9370 [31] for all but the five low-frequency vibrations.

[b] Potential Energy Distribution calculated for the TTT conformer.

[c] FR: Fermi resonance.

was found to be relevant for a proper mimetization of the (N)H···:N interactions. Indeed, the GGG conformer, where two interactions of this kind can occur simultaneously (Fig. 2), displays the largest energy lag between the 3-21G(N*) and the MP2/6-31G** values (Table 1). These hydrogen bonds were found to be of rather moderate strength, the NH···N distances calculated in the present work being 247 and 241 pm for conformers TGG' and GGG', respectively, that compare well with the microwave values of 264 and 252 pm [11].

In accordance with experimental results [10,11] and with previous theoretical studies on similar systems [5,20,26], values close to 115° and 109° for the CCN bond angles were obtained for those geometries displaying either a T or a G orientation of the nitrogen electron lone-pair relative to the C–C bond, respectively. In fact, the ab initio results now obtained are in good agreement with microwave [11] and electron diffraction studies [10], regarding both the geometrical parameters (NCCN$_{exp}$ = 63 ± 2° versus NCCN$_{calc}$(MP2/6-31G**) = 58.1°, for the most populated TGG' conformer) and the rotational constants ((A, B, C)$_{exp}$ = 14.355, 5.125, 4.356 GHz versus (A, B, C)$_{calc}$(MP2/6-31G**) = 14.281, 5.246, 4.427 GHz,

for the same conformer). As to the dipole moments, there is a fair agreement between the calculated (Table 1) and the experimental values [11] (μ_{exp} = 1.77 D versus μ_{calc}(MP2/6-31G**) = 2.21 D, and μ_{exp} = 2.20 D versus μ_{calc}(MP2/6-31G**) = 2.75 D, for GGG' and TGG' conformers, respectively). These values are in accordance with the well known positive deviation of the calculated dipole moments from the experimental values [30]. Although the ab initio results point to an inversion of the populations of the two most stable conformers, TGG' and GGG' (Table 1), relative to a previous microwave study [11], the rather small energy lag between them can easily explain this difference.

Inclusion of water solvent effects – SCRF approach – was found not to affect significantly the geometry of the conformers, but predicts a significant stabilisation of the ones displaying a higher dipole moment, and the symmetric arrangements, with a zero or next-to-zero dipole moment are clearly not favoured (Fig. 1) – e.g. conformer GGG (μ = 0.31 D) is destabilised by 5.1 kJ mol^{-1} relative to TGG (μ = 2.77 D). The asymmetric TGG' conformer was still found to be the most stable one at this level of calculation, displaying, however, a higher energy difference to

the next most populated conformation, GGG$'$ (3.13 versus 0.73 kJ mol^{-1}, Fig. 1).

3.2. Vibrational analysis

Fig. 3 shows the Raman spectra of 1,2-diaminoethane and 1,2-diaminoethane-N-d$_4$ for the solid, the pure liquid and the aqueous solution, in the 250–1700 cm^{-1} region. Experimental Raman wavenumbers of these systems are presented in Table 2, along with the calculated values (MP2/6-31G**level) for some conformers of the non-deuterated molecule. It was verified that the wavenumbers obtained at any level of calculation do not change by inclusion of the SCRF approach. The agreement between the experimental and calculated wavenumbers, using the recently proposed scaling factors of Scott and Radom [31], was found to be very good. Based on the calculated ab initio force field, a normal analysis was performed using local symmetry coordinates (available from the authors upon request). The potential energy distribution (Table 2) is rather localized, which supports the present choice of coordinates.

Usually, the spectral region below 600 cm^{-1} reflects any variation in the physical state of the sample, and is particularly useful when performing temperature-dependent conformational analysis [5–7]. In this study, however, no band intensity changes were detected when lowering the temperature from 25°C to 8°C, in the liquid state, because of the rather high melting point of this compound (8°C), that would ask for a broader temperature range to be investigated.

In the liquid phase, the Raman bands observed in the 250–600 cm^{-1} region – at 341, 473 and 512 cm^{-1} – correspond to CCN deformation oscillators, in agreement with previous assignments reported for *n*-propylamine [5]. This is corroborated by the shift of those signals to lower frequencies upon N-deuteration. Based on the normal coordinate analysis now undertaken, it is possible to assign the band at 473 cm^{-1} to TTT conformer, and the ones at 341 and 512 cm^{-1} to the conformations displaying a skeletal *gauche* arrangement.

In the solid sample, the band at 430 cm^{-1} corresponds to the NH$_2$ torsion, possibly overlapped in the liquid by the one at 340 cm^{-1}, while the band at 470 cm^{-1} confirms the presence of only the TTT

conformer in this phase. In aqueous solution this band is also clearly detected while the ones corresponding to *gauche* arrangements seem to disappear (Fig. 3).

From the normal coordinate results, the bands at 878, 976 and 1086 cm^{-1} are ascribed to the conformers displaying a G orientation around the NCCN dihedral angle, namely to the most stable ones TGG$'$ and GGG$'$. These bands are not observed either in the solid sample or in the aqueous solution, which reflects the absence of those arrangements in the first case, or their very small population, in the second. Similarly, on N-deuterated system the bands at 880 and 932 cm^{-1} disappear in the solid state. Although the calculated wavenumbers agreeing better with the experimental ones are those assigned to conformer TGG$'$, the spectral evidence now obtained is not enough to exclude the presence of other conformational minima (e.g GGG$'$). All these bands are mainly ascribed to CN stretching modes, that were found to be rather sensitive to NH$_2$ deuteration, as they were observed to shift ca. 40 cm^{-1} to lower frequencies in the liquid.

The 1099 cm^{-1} band, assigned to conformer TTT, was detected in the solid sample at 1109 cm^{-1}, confirming the sole existence of this conformation in that phase (Fig. 3).

The bands due to the amine groups, in turn, are easily identified in the spectra, for they display clear frequency shifts upon deuteration. Thus, while the corresponding wagging, twisting and deformation modes occur at 841, 1245 and 1600 cm^{-1}, respectively, for 1,2-diaminoethane, the same oscillators are observed at 732, 1001 and 1200 cm^{-1} for 1,2-diaminoethane-N-d$_4$. These bands were found to be slightly shifted to higher frequencies upon solidification of the sample (Fig. 3).

4. Conclusions

The ab initio conformational energies obtained for 1,2-diaminoethane suggest that the most stable conformers, both for the isolated molecule and the aqueous solution, are the ones where intramolecular (N)H$\cdots$:N hydrogen bonds can occur (TGG$'$ and GGG$'$). The presence of such arrangements, displaying *gauche* skeletal orientations that favour

the formation of those stabilizing interactions, was also detected in the Raman spectra of both the non-deuterated and N-deuterated diamine, in the liquid phase, along with the all-*trans* conformer, In turn, its absence in the spectra of both the solid sample and the aqueous solution seems to indicate that the intermolecular interactions occurring in these systems are responsible for a marked change in the relative order of conformational stability predicted by ab initio methods. Indeed in aqueous solution the electrostatic effects that would favour the most polar conformations are overruled by the intermolecular hydrogen bonds formed with the solvent, that seem to prevail over the intramolecular interactions occurring in both the pure liquid and the gas.

Thus, although the ab initio calculations for the isolated molecule reproduce rather well the experimental data for the liquid phase, the results obtained with the SCRF are opposed to what is observed experimentally for the solution, as this method is based solely on dielectric characteristics of the solvent and does not consider the stabilising intermolecular H bonds.

The results now obtained clearly indicate the occurrence of distinct conformers in the liquid phase for this polyamine, varying in the central dihedral angle, as well as in the orientation of the nitrogen electron lone pairs. Thus, unlike in the solid phase, the conformational behaviour of this system is determined, in the liquid, by the possibility of formation of stabilising intramolecular hydrogen bonds, while in aqueous solution it seems to be less dependent on the dielectric characteristics of the solvent than on its capability to form specific intermolecular water–amine interactions.

Acknowledgements

References

[1] R.O. Duthaler, J.D. Roberts, J. Am. Chem. Soc. 100 (1978) 3889.

[2] J.J.C. Telxeira-Dias, L.A.E. Batista de Carvalho, A.M. Amorim da Costa, I.M.S. Lampreia, E.F.G. Barbosa, Spectrochim. Acta 42A (1986) 589.

[3] L.A.E. Batista de Carvalho, A.M. Amorim da Costa, J.J.C. Telxeira-Dias, E.F.G. Barbosa, I.M.S. Lampreia, J. Raman Spec. 18 (1987) 115.

[4] A.M. Amorim da Costa, L.A.E. Batista de Carvalho, J.J.C. Teixeira-Dias, E.F.G. Barbosa, I.M.S. Lampreia, Can. J. Chem. 65 (1987) 384.

[5] L.A.E. Batista de Carvalho, A.M. Amorim da Costa, M.L. Duarte, J.J.C. Teixeira-Dias, Spectrochim Acta 44A (1988) 723.

[6] L.A.E. Batista de Carvalho, A.M. Amorim da Costa, J.J.C. Teixeira-Dias, J. Molec. Struct. 218 (1990) 105.

[7] L.A.E. Batista de Carvalho, J.J.C. Telxeira-Dias, J. Raman Spec. 26 (1995) 653.

[8] S. Jamet-Delcroix, Acta Cryst. B29 (1973) 977.

[9] R. Righini, S. Califano, Chem. Phys. 17 (1976) 45.

[10] A. Yokozeki, K. Kuchitsu, Bull. Chem. Soc. Jpn. 44 (1971) 2926.

[11] K.M. Marstokk, H. Mollendal, J. Molec. Struct. 49 (1978) 221.

[12] A. Sabatini, S. Califano, Spectrochim. Acta 16 (1960) 677.

[13] A. Diot, T. Theophanides, Can. J. Spec. 17 (1972) 67.

[14] Y. Omura, T. Shimanouchi, J. Mol. Spectrosc. 57 (1975) 480.

[15] M.G. Giorgini, M.R. Pelleti, G. Palliani, R.S. Cataliotti, J. Raman Spec. 14 (1983) 16.

[16] L. Radom, W.A. Lathan, W.J. Hehre, J.A. Pople, J. Am. Chem. Soc. 95 (1973) 693.

[17] K. Rasmussen, C. Tosi, Acta Chem. Scand. A37 (1983) 77.

[18] C. Van Alsenoy, K. Siam, J.D. Ewbank, L. Schater, J. Mol. Struct. (Theochem.) 136 (1986) 77.

[19] S.J. Lee, B.J. Mhin, S.J. Cho, J.J. Lee, K.S. Kim, J. Phys. Chem. 98 (1994) 1129.

[20] L.A.E. Batista de Carvalho, J.J.C. Teixeira-Dias, J. Mol. Struct. (Theochem) 282 (1993) 211.

[21] GAUSSIAN 94, Revision B 2, M.J. Frisch et al., Gaussian Inc., Pittsburgh PA, 1995.

[22] W.J. Hehre, R.F. Stewart, J.A. Pople, J. Am. Chem. Soc. 51 (1969) 2657.

[23] W.J. Hehre, R. Ditchfifield, R.F. Stewart, J.A. Pople, J. Am. Chem. Soc. 52 (1970) 2769.

[24] J.S. Binkley, J.A. People, W.J. Hehre, J. Am. Chem. Soc. 102 (1980) 939.

[25] M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pletro, W.J. Hehre, J. Am. Chem. Soc. 104 (1982) 2797.

[26] L.A.E. Batista de Carvalho, A.M. Amorim da Costa, J.J.C. Teixeira-Dias, J. Molec. Struct. (Theochem) 205 (1990) 327.

[27] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.

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

[29] M.W. Wong, K.B. Wiberg, M.J. Frisch, J. Am. Chem. Soc., 114 (1992) 1645 and references therein.

[30] W.J. Hehre, L. Radom, P.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, John Wiley and Sons, 1986.

[31] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.