

UDC 539.19;547.433;544.142.4

THEORETICAL STUDY OF STRUCTURE, STABILITY AND INFRARED SPECTRA OF HYDROGEN BONDING COMPLEXES PAIRING N-NITROSODIETHANOLAMINE (NDELA) AND ONE TO FIVE WATER MOLECULES

© 2008 R. Alizadeh*, N.M. Najafi

*Department of Chemistry, Faculty of Science, Shahid Beheshti University G.C., Evin, Tehran, Iran**Received December, 14, 2007*

A theoretical study of the interaction between N-nitrosodiethanolamine (NDELA) molecule and one to five molecules of water has been performed at the B3LYP level using a large polarized basis set. The calculated complexation energies (corrected for BSSE and ZPVE) of NDELA with one, two, three, four and five molecules of water are -4.62 , -9.83 , -15.29 , -21.60 , and -25.10 kcal/mol respectively at the B3LYP/6-311++G** level. In all complexes studied there are red shifts in the vibrational frequencies of the O—Hs of NDELA and water molecules along with increases in the corresponding IR intensities.

Keywords: hydrogen bond, clusters, nitrosamine, computations, B3LYP.

INTRODUCTION

Nitrosamines are both mutagenic and carcinogenic and widely present in the environment [1]. They have actions on the liver, kidney and lung. Humans have been exposed to these compounds in many ways, including food, rubber materials and waste water. These compounds have been detected at ppb levels in a wide variety of products such as bacon, ham, frankfurters, sausages, cheese, beer, rubber, ground water, smoked tobacco, tobacco, cosmetics, etc. [2–10].

N-nitrosodiethanolamine (NDELA) is considered of especially high risk to human health because of its presence in high concentrations. Children might be especially susceptible to the effects of this compound due to their low body weight, immature enzymatic system and weak gastric acidity [2].

NDELA can be formed from diethanolamine or triethanolamine reacting with nitrite or with nitrous gas in the work place environment. Diethanolamine and triethanolamine are often components of commercial cutting fluids used for neutralization and for emulsification purposes. Nitrite is sometimes added to cutting fluids for rust protection but also is found in the water used to dilute the cutting fluids [11].

Hydrogen bonding is an important phenomenon in many chemical and biological systems, and hydrogen bonded complexes have been extensively studied by a wide range of experimental techniques [12–14] and calculations [15]. A large number of molecules form hydrogen bonding complexes [16–23] in the form of DH-A where DH is a proton donor and A is an acceptor which usually has lone pair, unpaired electron, or π -electrons. The existence of OHs and N=O functional groups in NDELA (see Fig. 1, a) provide conditions for hydrogen bond formation between NDELA and other molecules such as H₂O that act as both hydrogen bond donors and acceptors.

The relatively high concentration of water throughout biological environments makes its interaction with other molecules important. Despite the potential importance of both H₂O and NDELA, to our knowledge there is no available in the literature either theoretical or experimental studies of the possible interactions of H₂O and NDELA. In the absence of experimental information, a theoretical analysis

* E-mail: r_alizadeh2005@yahoo.com

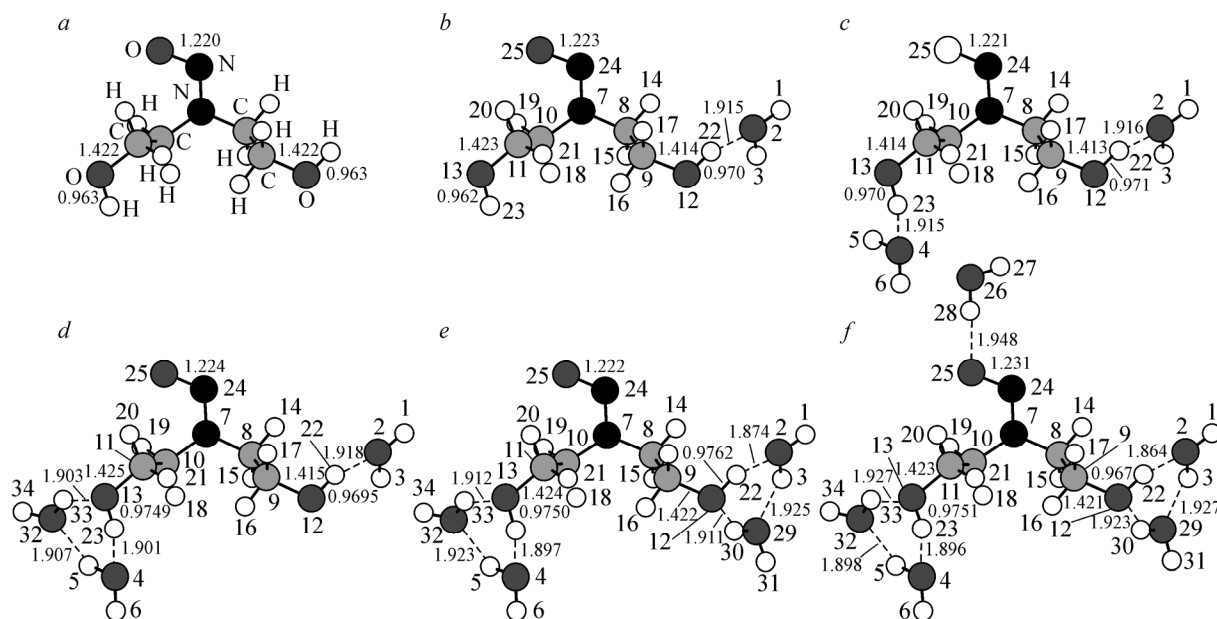


Fig. 1. B3LYP/6-311++G** optimized structures of (a) NDELA, (b) NDELA—H₂O, (c) NDELA—(H₂O)₂, (d) NDELA—(H₂O)₃, (e) NDELA—(H₂O)₄ and (f) NDELA—(H₂O)₅ complexes

of such complexes and their properties is in order. The present work reports a detailed examination of the stabilities, electronic structure, and vibrational frequencies of the title complexes for the first time.

COMPUTATIONAL METHODS

Calculations were performed using the Gaussian-03 system of codes [24]. The geometries of the isolated NDELA and H₂O moieties and their complexes were fully optimized at the B3LYP computational level using 6-311++G** basis set. Harmonic vibrational frequency calculations confirm the structures as minima and allow the evaluation of the zero-point vibrational energies (ZPVE). The counterpoise (CP) procedure was used to correct the interaction energy for basis set superposition error (BSSE) [25].

RESULTS AND DISCUSSION

Five structures corresponding to the minima located on the potential energy surfaces of the complexes at the B3LYP/6-311++g** computational level are shown in Fig. 1. Relevant geometry parameters characterizing all minima at B3LYP/6-311++G**, are shown in Table 1.

In the 1:1 complex of NDELA and water (Fig. 1, b), the water molecule acts as a proton acceptor and is bonded to one of the OH of NDELA. Comparison between geometrical parameters of the resulting complex and the monomers shows 8 mÅ lengthening of the OH bond (O₁₂—H₂₂) of NDELA.

In the 1:2 complex between NDELA and water molecules (Fig. 1, c), the second water molecule is a hydrogen bond acceptor and is bonded to another OH of NDELA. Comparison of the geometrical data of this complex and the monomers shows elongation of both OHs (O₁₂—H₂₂ and O₁₃—H₂₃) of NDELA by about 8 mÅ.

The 1:3 complex of NDELA and water (Fig. 1, d) was created by the addition of one molecule of water to the previously optimized structure of the 1:2 complex. In this 1:3 complex, consistent with the 1:2 complex, both OHs of NDELA act as HB donors and both H₂O molecules as HB acceptor. The newly added H₂O molecule has a dual role as an HB donor and an HB acceptor simultaneously. Indeed, the new H₂O molecule is an HB donor (H₃₃) to one of the OH of NDELA and an HB acceptor (H₅) from one of the H₂O molecules. Comparison of OH bond length in NDELA and the water monomers with the corresponding values in the 1:3 complex shows elongation of this parameter. Indeed, OH of two waters that are HB donor and HB acceptor (O₄—H₅ and O₃₂—H₃₃) are elongated

Table 1

Calculated bond lengths (Å) of complexes at B3LYP/6-311++G** level (see Fig. 1, a)

Functional groups	Bond lengths (Å)					
	Structure 1a	Structure 1b	Structure 1c	Structure 1d	Structure 1e	Structure 1f
N ₂₄ =O ₂₅	1.220	1.223	1.221	1.224	1.222	1.231
O ₁₂ —H ₂₂	0.963	0.970	0.971	0.969	0.976	0.976
O ₁₃ —H ₂₃	0.963	0.962	0.970	0.974	0.975	0.975
C ₉ —O ₁₂	1.422	1.414	1.413	1.414	1.422	1.420
C ₁₁ —O ₁₃	1.422	1.423	1.414	1.425	1.424	1.423
N ₇ —N ₂₄	1.339	1.336	1.327	1.334	1.336	1.321
N ₇ —C ₁₀	1.466	1.465	1.460	1.465	1.466	1.468
N ₇ —C ₈	1.458	1.459	1.466	1.460	1.459	1.461
C ₈ —C ₉	1.535	1.536	1.551	1.535	1.535	1.535
C ₁₀ —C ₁₁	1.537	1.537	1.540	1.537	1.537	1.538
O ₂ —H ₂₂	—	1.915	1.916	1.918	1.834	1.863
O ₂₅ —H ₂₈	—	—	—	—	—	1.947
O ₁₂ —H ₃₀	—	—	—	—	1.911	1.923
O ₄ —H ₂₃	—	—	1.915	1.901	1.896	1.895
O ₁₃ —H ₃₃	—	—	—	1.903	1.912	1.926
O ₂₉ —H ₃	—	—	—	—	1.925	1.926
O ₃₂ —H ₅	—	—	—	1.907	1.923	1.898
O ₂ —H ₁	—	0.963 (0.962*)	0.962	0.962	0.961	0.961
O ₂ —H ₃	—	0.963 (0.962*)	0.961	0.962	0.975	0.975
O ₄ —H ₅	—	—	0.963	0.975	0.976	0.976
O ₄ —H ₆	—	—	0.963	0.961	0.961	0.961
O ₂₉ —H ₃₀	—	—	—	—	0.975	0.975
O ₂₉ —H ₃₁	—	—	—	—	0.961	0.961
O ₃₂ —H ₃₃	—	—	—	0.976	0.976	0.975
O ₃₂ —H ₃₄	—	—	—	0.961	0.961	0.961
O ₂₆ —H ₂₇	—	—	—	—	—	0.961
O ₂₆ —H ₂₈	—	—	—	—	—	0.971

* Bond length in H₂O monomer.

about 14 mÅ due to complex formation. The lengthening OH (O₁₃—H₂₃) of NDELA interacting with two water molecules of about 12 mÅ is more than that of the OH (O₁₂—H₂₂) of NDELA interacting with a water molecule (7 mÅ elongation).

Fig. 1, *e* shows a 1:4 complex of NDELA and water molecules which is obtained by addition of one molecule of water to the optimized structure of the 1:3 complex. In this complex, both H₂O molecules and the OHs of NDELA act as HB donors and acceptors leading to cyclic hydrogen bonded complexes. Table 1 shows that bond length of both OHs of NDELA and the OHs of the interacting waters are lengthened by about 14 mÅ.

As shown in Fig. 1, *f*, the 1:5 complex of NDELA and water is established by addition of a new molecule of water interacting with N=O of NDELA. The hydrogen bond length between the H atom of the newly added water and N=O of NDELA is larger (1.947 Å) than other hydrogen bond lengths, for instance that containing O₃₂—H₅ (1.898 Å). In consistency with the general feature of hydrogen bonding interactions in this complex, elongation of all OHs takes part. For instance, the OH length with N=O is 9 mÅ and for other OHs the lengths are about 14 mÅ longer.

Table 2

Interaction energies E_{int} (kcal/mol) of studied complexes at different correction modes

Method	E_{int}				
	Structure 1b	Structure 1c	Structure 1d	Structure 1e	Structure 1f
B3LYP/6-311++G**	-6.55	-14.90	-24.46	-34.85	-40.61
ZPVE corrected	-4.92	-11.69	-18.11	-25.32	-29.40
BSSE corrected	-5.61	-13.04	-21.64	-31.13	-36.30
ZPVE+BSSE corrected	-3.98	-9.83	-15.29	-21.60	-25.10

Table 3

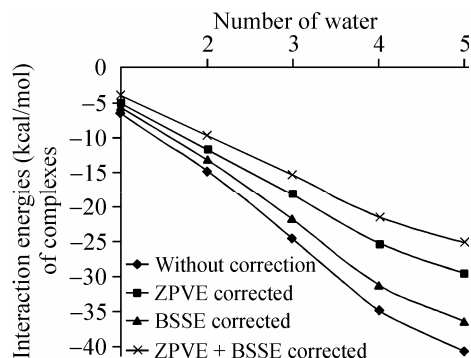
Vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of complexes at B3LYP/6-311++G** level

Assignment	Structure 1a		Structure 1b		Structure 1c		Structure 1d		Structure 1e		Structure 1f	
	ν	Int.	ν	Int.	ν	Int.	ν	Int.	ν	Int.	ν	Int.
C ₁₀ —N ₇ —N ₂₄ (sym.) St.	895	20	898	17	891	10	899	19	898	22	902	14
C ₁₁ —O ₁₃ (St.)	1057	214	1058	100	1076	223	1062	128	1063	175	1064	141
C ₉ —O ₁₂ (St.)	1057	214	1084	103	1084	10	1084	62	1072	66	1076	13
C ₁₀ —C ₁₁ (St.)	1058	8	1047	75	1025	6	1032	7	1033	10	1029	3
C ₈ —C ₉ (St.)	1058	8	1029	23	999	13	1028	34	1028	46	1036	10
C ₈ —N ₇ —C ₁₀ (asym.) St.	1287	3	1288	0.13	1275	20	1291	26	1293	26	1294	10
O ₁₃ —H ₂₃ (St.)	3830	20	3829	28	3698	466	3630	469	3627	450	3325	538
O ₁₂ —H ₂₂ (St.)	3830	48	3697	437	3704	202	3700	425	3566	67	3562	158
N ₇ —N ₂₄ —O ₂₅ (bend)	726	4	727	5	725	8	727	12	726	14	732	20
H ₁ —O ₂ —H ₃ (asym.) St.	—	—	3917	93	3891	103	3918	92	3896	72	3895	64
			3922*	57*								
H ₁ —O ₂ —H ₃ (sym.) St.	—	—	3816	15	3815	368	3817	14	3637	518	3640	563
			3818*	9*								
H ₃₃ —O ₃₂ —H ₃₄ (asym.) St.	—	—	—	—	—	—	—	—	3895	99	3894	113
H ₃₀ —O ₂₉ —H ₃₁ (asym.) St.	—	—	—	—	—	—	3616	714	3893	113	3893	114
H ₅ —O ₄ —H ₆ (asym.) St.	—	—	—	—	3911	90	—	—	3891	83	3890	81
H ₅ —O ₄ —H ₆ (sym.) St.	—	—	—	—	3812	15	3630	469	3626	450	—	—
H ₂₇ —O ₂₆ —H ₂₈ (asym.) St.	—	—	—	—	—	—	—	—	—	—	3889	95
H ₂₇ —O ₂₆ —H ₂₈ (sym.) St.	—	—	—	—	—	—	—	—	—	—	3681	578

* Vibrational frequencies in H₂O monomer.

The interaction energy of the complexes has been obtained from differences of the energies between the complexes and isolated monomers and the results are shown in Table 2. Calculated interaction energies have been corrected by BSSE and ZPVE. The trends in interaction energies due to addition of water molecules and the effect of the different corrections (BSSE and ZPVE) are shown in Fig 2. The relative stability of complexes at all computational levels are: $f > e > d > c > b$.

Fig. 2. Diagram of interaction energies for all complexes at the B3LYP/6-311++G**



Calculated vibrational frequencies and IR intensities of monomers and their five complexes at B3LYP/6-311++G** level are listed in Table 3. The stretching vibrational mode of OHs of NDELA (3698, 3704 cm^{-1}) which form hydrogen bonds with two molecules of water (Fig. 1, c) are found to be red shifted in comparison with the monomers (3830 cm^{-1}) and the IR intensities also have dramatically increased from 20 and 48 to 466 and 202 km/mol , respectively. Increasing the number of waters shows a larger red shift of the OH vibrational mode in the complexes. Fig. 3, b and Fig. 3, c show increasing red shift of OH stretching mode of NDELA due to complex formation with two and five molecules of water respectively. No significant frequency shifts for other NDELA atoms is predicted from these calculations. Formation of the hydrogen bonded complexes has little effect on other parts of NDELA molecule.

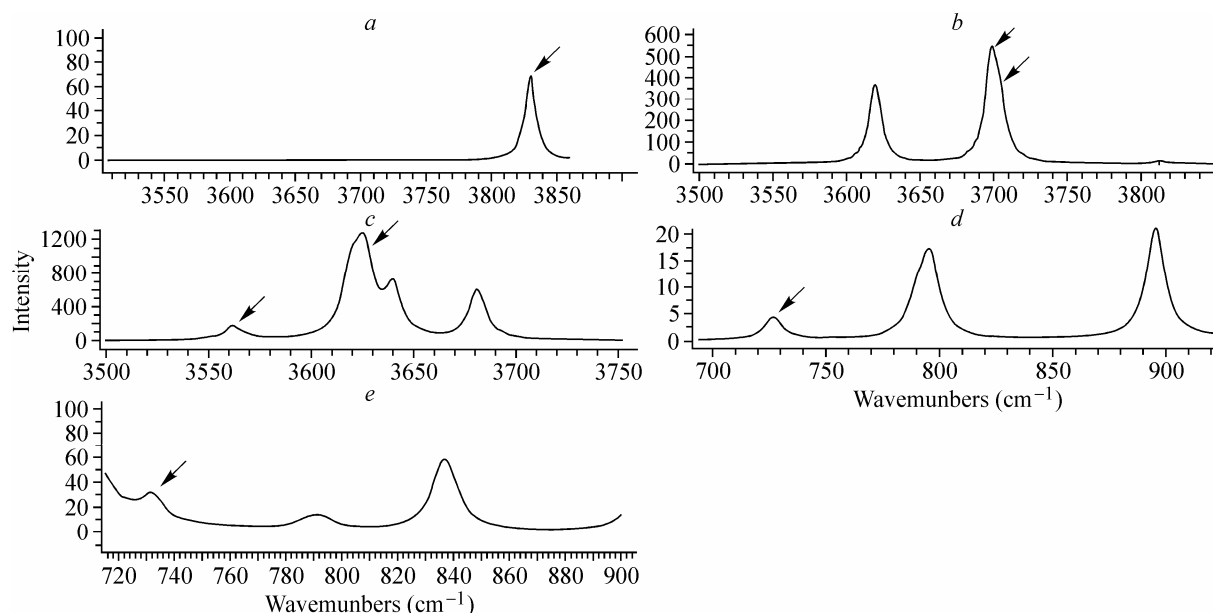


Fig. 3. Infrared spectra of (a) OH functional groups of NDELA, (b) OH functional groups of NDELA with two water molecules complex, (c) OH functional groups of NDELA with five water molecules complex, (d) N—N—O functional groups of NDELA, and (e) N—N—O functional groups of NDELA with five water molecules complex calculated at B3LYP/6-311++G**

ACKNOWLEDGEMENT

The authors thank Professor Mohammad Solimannejad from Arak University and Dr. Zahra Talebpour from Alzahra University for financial support of this research.

REFERENCES

1. You J., Fan X., Lao W. et al. // *Talanta*. – 1999. – **48**. – P. 437.
2. Zwickenkflug W., Ritcher E. // *J. Chromatogr. Sci.* – 1987. – **25**. – P. 506.
3. Oliveria C.P., Glória M.B.A., Barbour J.F., Scanlan R.A. // *J. Agric. Food Chem.* – 1995. – **43**. – P. 967.
4. Sen N.P., Seaman S.W., Baddoo P.A., Weber D. // *J. Food Sci.* – 1988. – **53**. – P. 731.
5. Maxwell R.J., Pensabene J.W., Fiddler W. // *J. Chromatogr. Sci.* – 1993. – **31**. – P. 212.
6. Tomkins B.A., Griest W.H. // *Anal. Chem.* – 1996. – **68**. – P. 2533.
7. Fine H.D., Ross R., Rounbehler D.P. et al. // *J. Agric. Food Chem.* – 1976. – **24**. – P. 1069.

8. *Sen N.P., Seaman S.W., Kushwaha S.C.* // J. Chromatogr. – 1989. – **463**. – P. 419.
9. *Glória M.B.A., Barbour J.F., Scanlan R.A.* // J. Agric. Food Chem. – 1997. – **45**. – P. 814.
10. *Stephany R.W., Freudenthal J., Egmond E. et al.* // Ibid. – 1976. – **24**. – P. 536.
11. *Spiegelhalder B., Preussmann R.* // J. Cancer Res. Clin. Oncol. – 1984. – **108**. – P. 160.
12. *Barone V., Palma P., Sanna N.* // Chem. Phys. Lett. – 2003. – **381**. – P. 451.
13. *Li Q.S., Fang W.H.* // Ibid. – **367**. – P. 637.
14. *Wang D., Chen S., Chen D.* // J. Photochem. Photobiol. A. – 2004. – **162**. – P. 407.
15. *Scheiner S.* // Hydrogen Bonding — A Theoretical Perspective, Oxford University Press, Oxford, 1997, and references therein.
16. *Pejov L., Solimannejad M., Stefov V.* // Chem. Phys. – 2006. – **323**. – P. 259.
17. *Solimannejad M., Scheiner S.* // Chem. Phys. Lett. – 2006. – **429**. – P. 38.
18. *Solimannejad M., Scheiner S.* // Ibid. – **424**. – P. 1.
19. *Solimannejad M., Scheiner S.* // J. Phys. Chem. – 2006. – **A110**. – P. 5948.
20. *Solimannejad M., Alkorta I.* // Ibid. – P. 10817.
21. *Solimannejad M., Alikhani M.E.* // Chem. Phys. Lett. – 2005. – **406**. – P. 351.
22. *Solimannejad M., Azimi G., Pejov L.* // Ibid. – 2004. – **400**. – P. 185.
23. *Solimannejad M., Pejov L.* // Ibid. – 2004. – **385**. – P. 394.
24. *Frisch M.J. et al.* // Gaussian-03, Revision B02, Gaussian, Inc., Pittsburgh, PA 2003.
25. *Boys S.F., Bernardi F.* // Mol. Phys. – 1970. – **19**. – P. 553.