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Theoretical Study of the Solvation of Nitrogen. Two Different Approaches

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Two different approaches were used for a theoretical study of the solvation of N_2, with HF, H_2O, NH_3, CH_4 as solvents. In the first approach, the contour maps of orientationally optimized interaction energy between N_2 and one solvent molecule were computed by fast semiempirical methods (Extended Hückel and CNDO/2) in order to find a reliable but not too expensive calculation method for solvation models. In the case of the N_2-H_2O system, an *ab initio* map was also evaluated for comparison. The second approach is based on the building up of clusters with one molecule of N_2 surrounded by a number (2 to 8) of solvent molecules and finding the structure of such clusters by energy minimization. From the structures obtained it results that they are determined mainly by steric factors, so that clusters optimized by means of different methods are similar, despite the remarkable differences in the maps.

Key words: Solvation of N_2 – Intermolecular potentials.

1. Introduction

Various theoretical investigations into solvation have been carried out over recent years.

Analytical potentials are often used in order to simulate the solvent and keep the enormous amount of calculations within reasonable limits [1]. In a usual approximation, neglecting many body contributions (generally relatively small), one needs the potentials describing the interaction not only between one solute/one solvent molecules but also between two solvent molecules. Potentials derived from *ab initio* calculations, in which water is the solvent and an enzyme, an aminoacid, a model molecule of biological interest, or a small molecule is the

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solute, are now available [1–8]. Alternatively, semiempirical quantum mechanical methods are chosen to examine structural problems involving the solvent. For example liquid water [9], the structural organization of water molecules in enzymes [10] and in DNA [11], and the role of solvents on electronic transitions [12] and on chemical reactions [13–15] have been investigated. In all cases it appears that water was the only solvent investigated.

In the course of our research on the solvent effect on organic reactions [15] the choice of the number of solvent molecules needed to describe the first shell of solvation adequately presented a major problem. In a recent paper [16] the interaction between a small apolar solute (N_2) and strongly polar solvents (H_2O and HF) was computed by the semiempirical CNDO/2 method. The interaction energy maps were compared with the structures of the clusters built up by one nitrogen molecule and a number (two to eight) of H_2O or HF molecules.

In the present study other solvents, such as ammonia and methane, and other computational techniques, were taken into consideration and the isoenergy contour maps of orientationally optimized N_2–solvent interactions (s. = H_2O, HF, NH_3, CH_4), computed by EHT and CNDO/2 methods, were obtained. The *ab initio* surface for the N_2—H_2O system was also computed.

We set ourselves two goals: first, to estimate the reliability of the semiempirical methods considered for predicting solute/solvent interactions by comparison with *ab initio* results; secondly, to compare the information given by the semiempirical interaction surfaces with those deduced from the solvent clusters obtained by directly surrounding one solute molecule with a few solvent units.

2. Calculations

The CNDO/2 method was employed following the standard procedure, with the parameters assigned by Pople and Segal [17–19]. EHT calculations were performed according to the early formulation by Hoffman [20]. In view of a close comparison between the two semiempirical methods the valence state ionization potentials and the Slater exponents necessary for EHT were the same as those adopted for CNDO/2. For *ab initio* LCAO-MO-SCF calculations the Gaussian minimal basis set (7/3) [21] and the IBMOL-6 program by Clementi *et al.* [22] were used. An energy minimization process following Powell's technique [23] was applied to optimize the geometrical parameters.

Table 1. Geometrical parameters of N_2 and of solvent molecules. Bond-lengths are in Å and angles in degrees

	N_2	HF	$H_2O(C_{2v})$		$NH_3(C_{3v})$		$CH_4(T_d)$
	N—N	H—F	O—H	$H\hat{O}H$	N—H	$H\hat{N}H$	C—H
exp	1.094[a]	0.917[b]	0.957	104.5[c]	1.012	106.7[d]	1.085[e]
CNDO/2	1.143	1.000	1.029	104.5	1.065	106.4	1.116

[a] Ref. (26); [b] Ref. (27); [c] Ref. (28); [d] Ref. (29); [e] Ref. (30, 31)

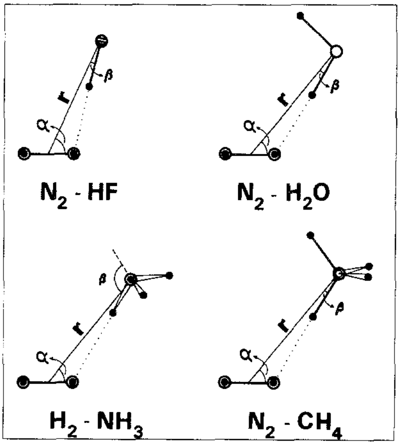


Fig. 1. Geometrical parameters defining the position of each solvent molecule relative to N_2. The angle γ, not depicted in the figure, is the smallest dihedral angle between the plane containing the three nitrogen atoms and the plane defined by r and one hydrogen atom

Throughout the calculations the interacting molecules were kept rigid. Optimized geometries were adopted in CNDO calculations, while experimental values were used for EHT and *ab initio* ones. The geometrical parameters adopted for N_2 and the solvents are reported in Table 1. The parameters defining the relative positions of the solvent molecules with respect to N_2 are r, α and β. As shown in Fig. 1, we define r as the distance between the center of mass of N_2 and the heavy atom of the solvent molecule; α is the angle between r and the N—N bond, and β is the minimum angle between r and the H—M bond ($M = F, O, N, C$) of the solvent molecule.

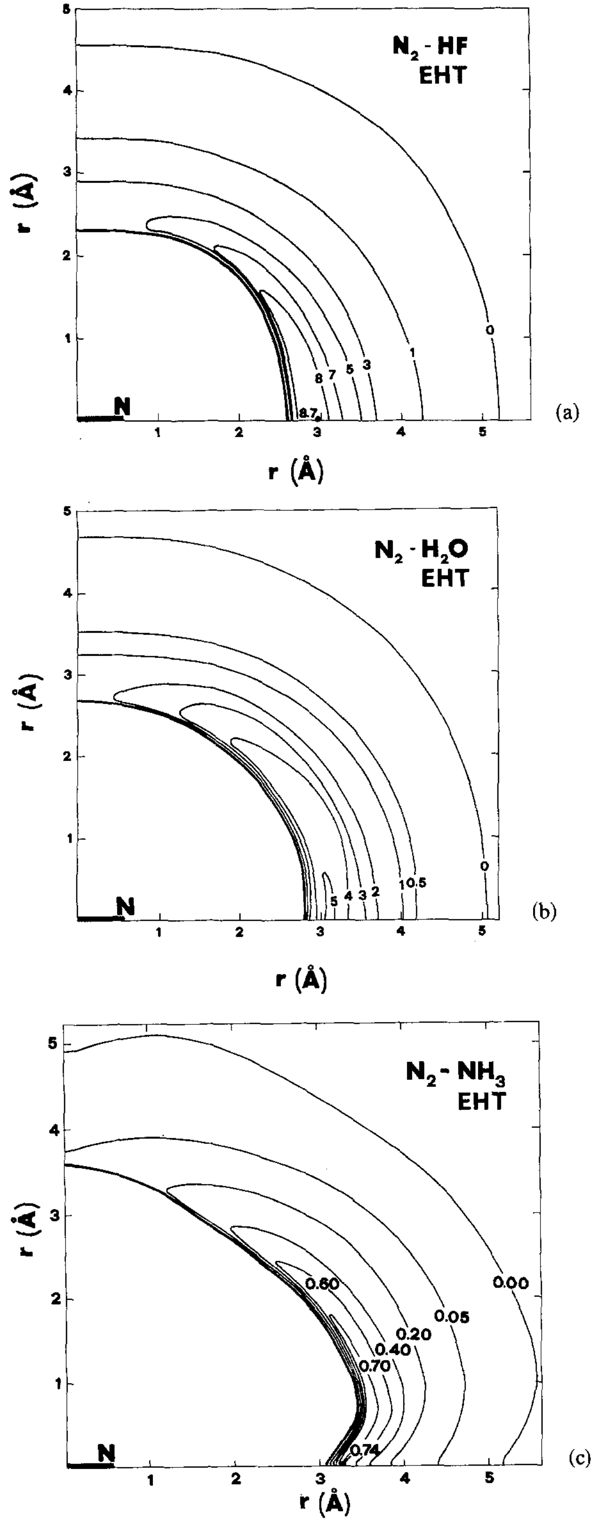
In the case of NH_3 a further parameter γ (i.e. the smallest dihedral angle between the plane containing the three nitrogen atoms and the plane defined by r and one hydrogen atom) was required in order to define the position of the solvent molecule.

3. Results

3.1. Energy Maps

The calculation of interaction energy contour maps is widely used in the study of solute–solvent interactions [8, 10, 24, 25]. Owing to the symmetry of $N_2(D_{\infty h})$ the maps were computed by taking into account a single quadrant of a plane defined by N_2 and the heavy atom of the solvent unit. In the quadrant, the solvent molecule was placed at regular distances (0.2 Å, for semiempirical calculations, 0.4 Å for *ab initio* ones) from the center of mass of N_2 in several directions. At each point the total energy of the solute–solvent system was minimized with respect to complete rotation of the solvent unit: H_2O and HF always resulted to be coplanar with N_2; CH_4 was found to be symmetric with respect to the map plane.

The interaction energy maps computed by CNDO/2 and EHT are shown in Fig. 2 and 3. The N_2—CH_4 map for the EHT method is not reported because a negligible interaction was found beyond the repulsive region. Common features are found in


N$_2$ - HF
EHT
r (Å)
r (Å)
0
1
3
5
7
8
8.7
N
(a)
N$_2$ - H$_2$O
EHT
r (Å)
r (Å)
0
0.5
1
2
3
4
5
N
(b)
N$_2$ - NH$_3$
EHT
r (Å)
r (Å)
0.00
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0.20
0.40
0.60
0.70
0.74
N
(c)
1
2
3
4
5

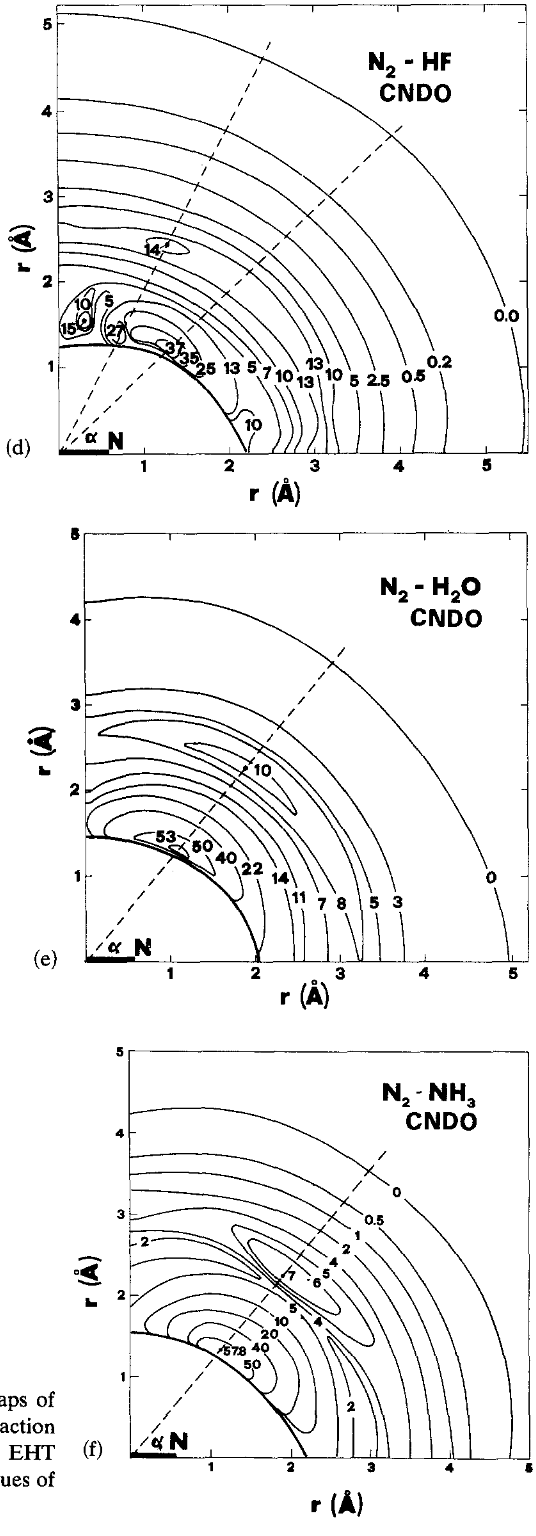

Fig. 2. Isoenergy (kcal/mole) contour maps of orientationally optimized N_2–solvent interaction energies, calculated by CNDO/2 and EHT methods for HF, H_2O, NH_3. Absolute values of attractive interaction energy are reported

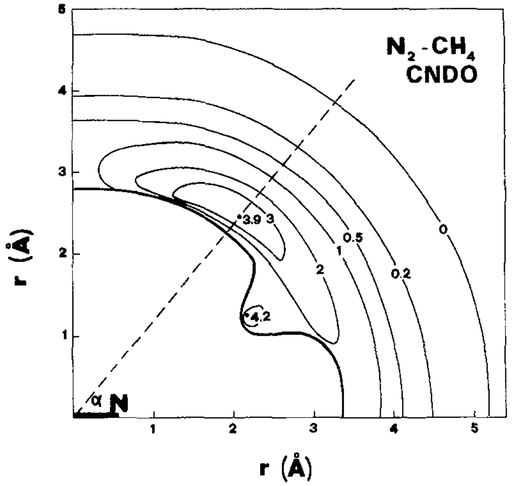

Fig. 3. Isoenergy (kcal/mole) contour map of orientationally optimized N_2—CH_4 interaction energies, calculated by CNDO/2 method. The corresponding map calculated by EHT is not reported, because the computed interactions are negligible. Absolute values of attractive interaction energy are reported

CNDO maps. First, two different kinds of minima can be observed in each map: an outer minimum which may be due to the solvation interaction, and other inner minima. The latter may be classified as "reactive" minima, owing to the strong interaction energy as well as to the short distance between the heavy atom of the solvent molecule and N_2. Moreover, the solvation minima are located at values of α ranging between 50° and 65° as reported in Table 2.

In EHT maps a single solvation minimum appears for $\alpha = 0°$, whereas the values of r are quite close to the corresponding ones for CNDO maps, as shown in Table 2.

In all solvation minima, regardless of the calculation method, the solvent molecule is oriented so that a H atom is pointing towards a N atom; the N—H distance is in the range of 1.5–1.7 Å; in other words a hydrogen bond may be hypothesised.

Table 2. Energy and molecular geometries in solvation minima of energy contour maps

	Method	Energy (a.u.)	E_{solv} (kcal/mol)	r(Å)	α(°)	β(°)	N···H(Å)
$N_2.HF$	CNDO	−51.5495	−14.00	2.71	65	10	1.52
	EHT	−10.9886	−8.75	2.95	0	0	1.46
$N_2.H_2O$	CNDO	−42.9980	−10.20	2.89	50	10	1.53
	EHT	−9.9393	−5.05	3.12	0	0	1.62
	ab initio	−184.2717	−1.59	3.85	0	9	2.38
		−184.2707	−0.92	3.56	50	43	2.50
$N_2.NH_3$	CNDO[a]	−37.0727	−7.00	2.93	50	107	1.72
	EHT[b]	−9.0924	−0.74	3.15	0	2	1.66
$N_2.CH_4$[c]	CNDO	−33.2127	−3.90	3.13	50	7	1.68
	ab initio	−148.5025	−0.13	4.80	0	0	3.21

[a] $\gamma = 30°$; [b] $\gamma = 0°$; [c] EHT interaction energy is negligible.

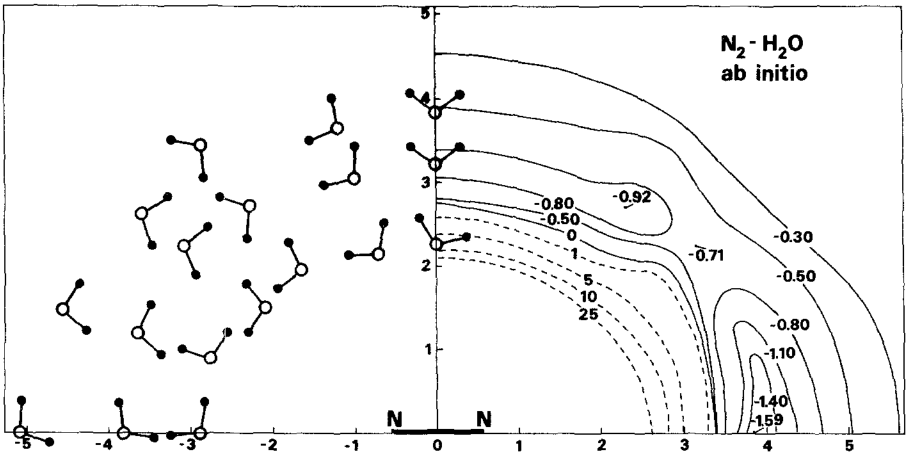

Fig. 4. *Ab initio* isoenergy contour map of orientationally optimized N_2—H_2O interaction energies (kcal/mole). The molecular geometry corresponding to a given energy is depicted in the left side of the figure. The size of the water molecules are scaled down to make the figure more legible

The *ab initio* map for the N_2—H_2O interaction (Fig. 4) shows two well-defined zones. The inner one is repulsive and extends as far as 3.0–3.5 Å from N_2. The outer part of the map is attractive and shows two minima. The absolute one lies along the direction of the N—N bond at $r = 3.85$ Å. The relative minimum falls at $\alpha = 50°$, $r = 3.56$ Å. The barrier between the two minima is about 1 kcal/mole. In the repulsive region the oxygen of the water molecule points towards the nitrogen atom. In the two minima, on the contrary, one hydrogen atom of water points towards the nitrogen molecule. However, from $\alpha = 0°$ to 90° the water molecule rotates and at about 90° the oxygen points towards N_2. The trends described are shown on the left side of Fig. 4. A comparison of semiempirical and *ab initio* results in the case of the N_2—H_2O system indicates that CNDO and EHT only partially describe the interaction. In particular, EHT does not reproduce the relative minimum at $\alpha = 50°$, while it gives a fairly correct description of the absolute minimum at $\alpha = 0°$; on the other hand, CNDO does not reproduce the absolute minimum, but gives a minimum at $\alpha = 50°$. As expected, the interaction energy is strongly overestimated by both methods (see Table 2). Indeed, even though experimental data about the solubility of N_2 are not available, the solvation energy of N_2 does not look like exceeding a few kcal/mole even in polar solvents. The present *ab initio* calculations for N_2 give a value of 1.59 kcal/mol, which can be considered acceptable if one takes into account that dispersion energy and other effects are not included in the calculation.

In the case of N_2—CH_4 system, while EHT gives only repulsive interactions, CNDO predicts two energy minima of about −4 kcal/mol as shown in Fig. 3. Since this result might be an artifact of the CNDO method, *ab initio* calculations have been performed for several configurations of N_2—CH_4: interactions resulted to be very weak, with negative values of energy (~ -0.13 kcal/mol) for $\alpha = 0°$ and $r \sim 4.8$ Å.

Both in CNDO and EHT maps a regular trend for the solvation interaction energy values is observed in going from HF to H_2O, NH_3, CH_4 solvents: the energy for more polar solvents is higher than for less polar or apolar ones, as is to be expected.

3.2. Clusters

Solute–solvent interactions have also been investigated by considering clusters built up from a molecule of solute surrounded by a number of solvent units simulating the first solvation shell. In order to compare the information obtained from the two different approaches, calculations on the structure of clusters including N_2 and 2, 4, 6, 8 molecules of HF and H_2O were performed using CNDO and EHT methods.

The geometrical parameters obtained by minimizing the total energy of the cluster are reported in Tables 3–4 and shown in Figs. 5 and 6. It is noteworthy that the simmetry of the clusters is itself a result of the calculation.

The geometries of the clusters obtained with the CNDO method differ from those obtained with EHT only when a small number (two) of solvent molecules (H_2O or HF) are considered, as evidenced in Tables 3 and 4. Indeed, the geometrical

Table 3. Energy and geometries of $N_2(H_2O)_n$ clusters. Distances in Å, angles in degrees

n	Method	Structure (Fig. 5)	E (a.u.)	ΔE (kcal/mol)	$\Delta E/n$ (kcal/mol)	r	α	β	$r(N\cdots H)$
2	CNDO	I	−62.9049	−20.0	−10.0	2.85	53	10	1.53
	EHT	II	−12.3730	−9.6	−4.8	3.14	0	2	1.56
4	CNDO	III	−102.7160	−38.0	−9.5	2.90	50	10	1.54
	EHT	III	−20.2727	−14.4	−3.6	3.08	40	12	1.68
6	CNDO	IV	−142.5232	−53.4	−8.9	2.86	55	10	1.55
	EHT	IV	−28.1699	−17.6	−2.9	3.07	43	9	1.73
8	CNDO	V	−182.3259	−66.4	−8.3	2.79	64	28	1.58
	EHT	V	−36.0638	−18.8	−2.4	3.08	49	10	1.80

Table 4. Energy and geometries of $N_2(HF)_n$ clusters. Distances in Å, angles in degrees

n	Method	Structure (Fig. 6)	E (a.u.)	ΔE (kcal/mol)	$\Delta E/n$ (kcal/mol)	r	α	β	$r(N\cdots H)$
2	CNDO	I	−80.0074	−27.2	−13.6	2.76	54	13	1.47
	EHT	II	−14.1504	−16.8	−8.4	2.94	0	0	1.48
4	CNDO	III	−136.9110	−46.0	−11.5	2.80	50	10	1.50
	EHT	III	−23.8218	−25.5	−6.3	2.83	39	12	1.51
6	CNDO	IV	−193.8071	−60.6	−10.1	2.82	50	10	1.52
	EHT	IV	−33.4897	−31.3	−5.2	2.81	47	14	1.55
8	CNDO	V	−250.6906	−66.4	−8.3	2.84	52	10	1.56
	EHT	V	−43.1525	−34.3	−4.3	2.81	53	14	1.60

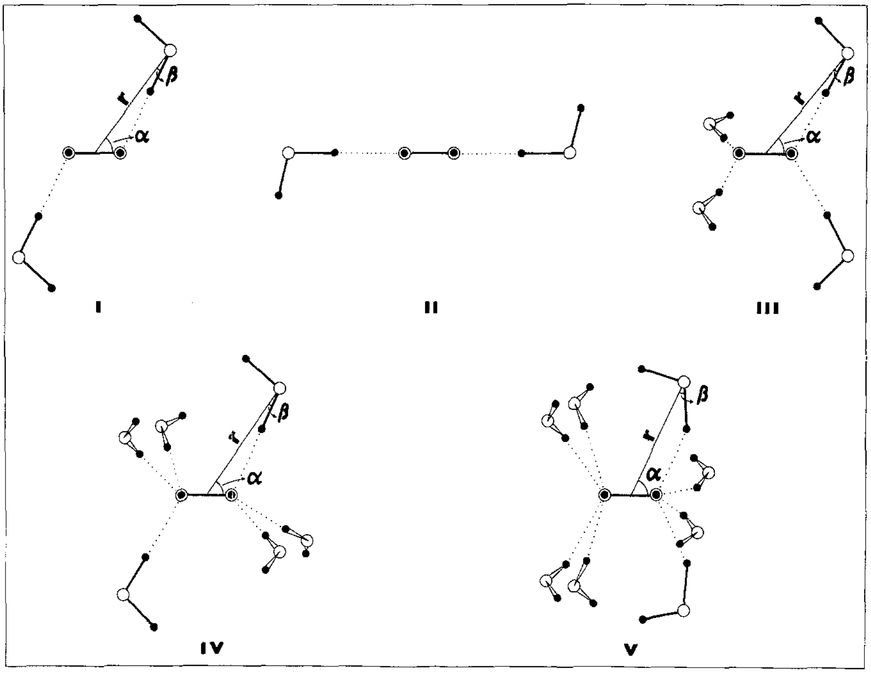

Fig. 5. Geometries and parameters of $N_2(H_2O)_n$ clusters ($n = 2, 4, 6, 8$). In the case of $n = 2$, I refers to CNDO/2 calculation, II to EHT, respectively

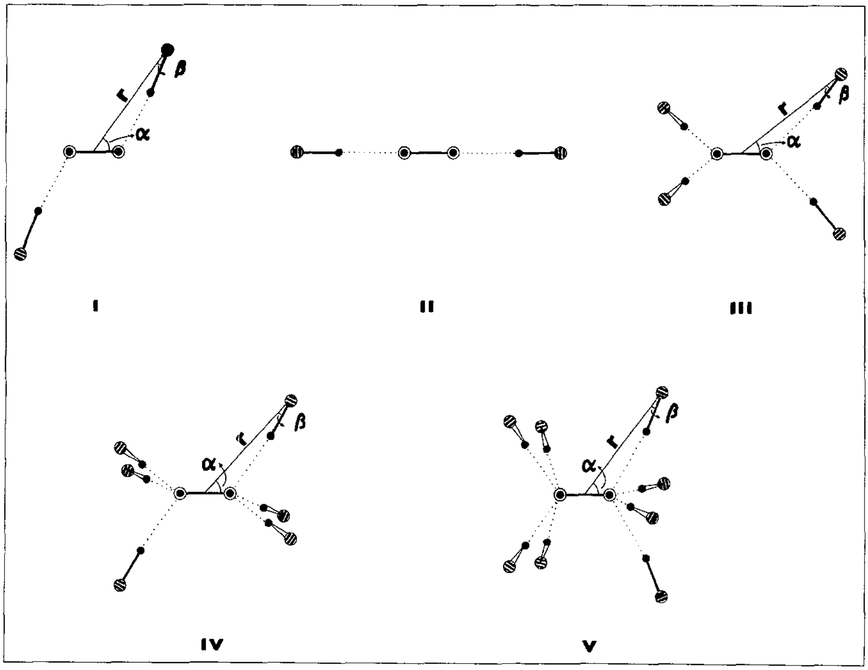

Fig. 6. Geometries and parameters for $N_2(HF)_n$ clusters (n = 2, 4, 6, 8). In the case of n = 2, I refers to CNDO/2 calculations, II to EHT, respectively

Table 5. Partition of the total energy[a] of the clusters $N_2(H_2O)_n$ and $N_2(HF)_n$ ($n = 2$–8), computed by CNDO/2 and EHT methods

Method	System	Structure	n	E_A	E_B	E_C	E_D[c]	E_F[c]
CNDO/2	$N_2(H_2O)_n$	I[b]	2	−62.9049	−39.7822	−23.1227	+0.0010	−0.0322
		III	4	−102.7160	−79.5667	−23.1493	−0.0003	−0.0588
		IV	6	−142.5232	−119.3463	−23.1769	+0.0033	−0.0864
		V	8	−182.3259	−159.1378	−23.1881	−0.0050	−0.0976
	$N_2(HF)_n$	I[d]	2	−80.0074	−56.8729	−23.1345	+0.0005	−0.0440
		III	4	−136.9110	−113.7421	−23.1689	+0.0048	−0.0784
		IV	6	−193.8071	−170.6083	−23.1988	+0.0119	−0.1083
		V	8	−250.6906	−227.4731	−23.2175	+0.0205	−0.1270
EHT	$N_2(H_2O)_n$	II	2	−12.3730	−7.8920	−4.4810	−0.0000	−0.0154
		III	4	−20.2727	−15.7845	−4.4882	−0.0005	−0.0226
		IV	6	−28.1699	−23.6764	−4.4936	−0.0004	−0.0280
		V	8	−36.0638	−31.5686	−4.4952	−0.0006	−0.0296
	$N_2(HF)_n$	II	2	−14.1504	−9.6581	−4.4923	−0.0001	−0.0267
		III	4	−23.8218	−19.3161	−4.5057	−0.0001	−0.0401
		IV	6	−33.4897	−28.9742	−4.5155	−0.0002	−0.0499
		V	8	−43.1525	−38.6322	−4.5203	−0.0002	−0.0547

[a] Energy in a.u.: E_A total energy of the clusters; E_B: energy of the solvent units; $E_C = E_A - E_B$, solute/solvent plus nitrogen energy; $E_D = E_B - n.E_{H_2O}$, energy difference between the solvent cluster and a corresponding number of isolated water molecules; $E_F = E_C - E_{N_2}$, solute/solvent interaction.

[b] see Fig. 5; [c] $E(N_2) = -23.0905$ (CNDO), -4.4656 (EHT); $E(HF) = -28.4367$ (CNDO), -4.8290 (EHT); $E(H_2O) = -19.8912$ (CNDO), -3.9460 (EHT); in a.u. [d] see Fig. 6.

parameters *r*, α, β, for the cluster including two solvent units are close to the corresponding ones defining the preferred positions of the solvent in the interaction maps. For higher coordination numbers the clusters optimized with the two semiempirical methods are similar. This finding is probably due to the repulsive interactions among solvent molecules: in the case of the larger clusters, when the number of solvent units surrounding each nitrogen atom is increased, they lie in staggered planes according to the decrease in solvation energy for molecule (Tables 3 and 4).

To get further insight in the relative stability of the different clusters a partition of the total energy was undertaken. In this view the energy of the solvent molecules alone, fixed at the position optimized for the different clusters, have been computed (see column B in Table 5). Column A of the same Table gives the total energy, while in column C the energy difference E_A–E_B, representing the sum of the energy of the isolated nitrogen molecule and the solute/solvent interactions, is reported. In column D the difference between the energy of the water cages (E_B) and that of a corresponding number of isolated water units is shown. Finally column E lists the energy of solute–solvent interactions obtained by subtracting the energy of the isolated nitrogen molecule from E_C.

The data collected in Table 5 put in evidence two interesting points. Firstly the binding energies of solvent clusters (E_D) are very small, and in the most clusters calculated by CNDO/2 method are destabilizing. On the other hand it appears that the stability of the clusters is mainly due to solvent/solute interaction (E_F) which regularly increases as the number of solvent units increases. In this sense, in spite of the overestimation of solvation energies put in evidence in Table 2 one can say that the stability of the clusters increases with the number of the added solvent units, at least in the case under study (two–eight water molecules taken into consideration).

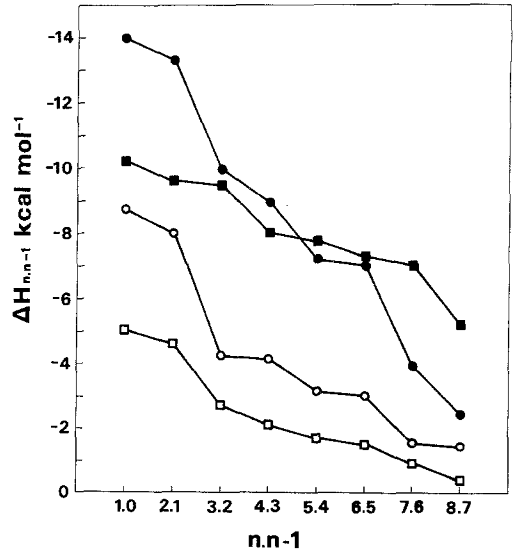

Fig. 7. Calculated values of $\Delta H_{n,n-1}$ for successive additions of solvent molecules to N_2; ●: HF(CNDO/2); ○: HF(EHT); ■: H_2O(CNDO/2); □: H_2O(EHT)

The trend of solvation energy and calculated values of $\Delta H_{n,n-1}$ describing subsequent additions of solvent molecules to N_2, shown in Fig. 7, shows that a reasonable coordination number for N_2 would be eight, so that, according to the present calculations, the first solvation shell of N_2 would include eight molecules.

4. Discussion

The present results, regarding neutral molecules in polar solvents furnish further information about the applicability of semiempirical methods to the calculation of solute–solvent interactions. With this in view, an *ab initio* calculation for the N_2—H_2O system was performed in order to make a direct comparison with other methods. Firstly, it appears evident that the interaction energy maps for one solute - one solvent molecules obtained with the CNDO/2 method show an absolute minimum, defined above as the "reactive" one which does not match the position of the absolute minimum found using *ab initio* calculations in the case of the N_2—H_2O system.

The CNDO/2 absolute minimum is probably a side effect of this method which strongly overestimates bonding interactions (see for example Ref. 9 where a similar case is reported). Furthermore, EHT interaction energy maps fail to describe the relative minimum found in *ab initio* map for the N_2—H_2O system. Moreover, both method overestimate the interaction energy value.

As for the clusters, when only two solvent molecules are considered, CNDO and EHT results do not correspond. However,the geometry of CNDO and EHT clusters become equivalent when a larger number of solvent molecules are included in the calculation to describe the first shell of solvation. Moreover, in this case the positions of the solvent molecules are compatible with the results of *ab initio* calculations, as they correspond roughly to the relative minimum of the *ab initio* map. When a large number of solvent units are included, it seems that the positions of the molecules are more influenced by steric hindrance than by electronic interactions. We therefore feel that semiempirical methods may be safely used to describe the positions preferred by the solvent molecules of the first shell of solvation with respect to the solute considered, even though we are well aware that a cluster with eight solvents molecules represents the lowest threshold for the reliable simulation of the solvation.

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