Intermolecular hydrogen bonding in NLO. Theoretical analysis of the nitroaniline and HF cases

Vicente Moliner,[a] **Purificación Escribano**[b] **and Eduardo Peris***[,b]

[a] *Departament de Ciències Experimentals, Universitat Jaume I, 12080 Castellón, Spain*
[b] *Departament de Química Inorgànica i Orgànica, Universitat Jaume I, 12080 Castellón, Spain*

Monomer and dimer structures of *p*-nitroaniline have been theoretically optimized both *in vacuo* and in the presence of an electric dipole field by means of *ab initio* molecular orbital procedures at the Hartree–Fock level of theory with the 6-31G and 6-31 + G** basis sets. The electron correlation has been estimated at the MP2/6-31 + G** level and by calculations based on density functional theory (B3LYP/6-31 + G**). The hydrogen-bonded structure of the dimer has been studied in detail and H bond energies of 2.5–5.7 kcal mol^{-1} have been obtained. The hyperpolarizabilities have been also estimated at all levels of calculation and a clear increase in the value of β has been observed in going from the monomer to the dimer structure. A similar study has been performed in H-bonded chains of HF. The theoretical study of the HF chains leads to no increase in the value of β, while the hypothetical linear structure clearly leads to an increase of this value with the number of molecules in the cluster. The dependence of the geometries of the stationary structures and the nonlinear optical (NLO) properties upon theoretical methods is discussed. This analysis suggests that the hyperpolarizabilities strongly depend on the number of molecules aggregated through H bonds. We have now shown that connecting molecules *via* intermolecular hydrogen bonding, especially when this gives rise to a linear structure, must be considered as a useful second way of linking donor and acceptor.

During the last decade, a great deal of work has been carried out in the investigation of the nonlinear optical properties of many different types of materials. Much of this effort has been dedicated to rationalizing new methods of designing chromophores with large quadratic hyperpolarizabilities.[1] Some attention has also been paid to the role of intermolecular interactions in nonlinear optical materials[2,3] but, in fact, most of the efforts in this field have been focused on the design and characterization of molecules that crystallize with an acentric crystal packing, in order to get nonzero values of the macroscopic polarization χ.[4] In this sense, many strategies for forming noncentrosymmetric crystals capable of showing SHG (second harmonic generation) activity have employed steric hindrance,[2a] dipole–dipole interaction reduction,[2e] and hydrogen bonding.[3] Few studies have examined how pairs, trimers, or clusters of molecules differ in their β property from the individual molecules, although the effect of intermolecular charge transfer has been suggested to increase β for linear clusters.[3a,e]

Nitroanilines have inherently large second-order microscopic polarizabilities and they seem to be very good candidates for nonlinear optical materials.[5] As far as we know, there has been only one attempt to systematically explore the second-order nonlinear response of clusters of these chromophores to relate the resulting intermolecular interactions to the quadratic hyperpolarizabilities,[6] these molecular interactions being of the dipole–dipole type. In very detailed work, Etter and coworkers[3d] have shown that hydrogen-bond interactions play an important role in the packing patterns of nitroanilines, considering that this type of interaction can help in predicting the orientations of neighbouring nitroaniline molecules.

Computational calculations of β have also recently received increasing attention,[5–7] developing to a point that, in most cases, the theoretical values are very close to the experimental ones. In a very recent review,[1f] Long has summarized a two-step model concerning electronic properties that has been important in predicting the usefulness of new NLO materials. This approach suggests that molecules must possess (*a*) excited states close in energy to the ground state, (*b*) large oscillator strengths for electronic transitions from ground to excited states and (*c*) a large difference between the ground and the excited state dipole moments. These requirements are best found in systems showing charge transfer between electron-donating and electron-withdrawing groups. We find from the literature that the computed β values for *p*-nitroaniline are among the most inaccurate ones, in each case falling below the experimental ones.[5a] It is important to point out that the experimental values of β for the *o*- and *m*-nitroanilines are much lower than that observed in the *para* isomer and the theoretical data for these are in much better agreement with the experimental ones.[5e] We believe that the reason for the disagreement between the theoretical and experimental results in *p*-nitroaniline is mainly due to molecular association through hydrogen bonding, which has never been considered in the theoretical simulation. Obviously, higher levels of theory would give more accurate results (*i.e.*, solvent effects have rarely been studied, correlation can be taken into account by MP4 or CI and the basis set can always be extended) but, in any case, the correct molecular model has to be chosen. Hydrogen bonding can also occur in the *meta* and *para* isomers of nitroaniline, but the associated systems do not give rise to a linear arrangement that could increase the nonlinear response. In this paper, we present a detailed computational analysis of hydrogen bonding in *p*-nitroaniline and its effect on the value of the quadratic hyperpolarizability, β. The dependence of β on H bonding has also been studied in a simpler molecule like HF, where head-to-tail hydrogen bonding is well documented.

As far as we know, this is the first detailed report that hydrogen bonding has a clear effect on increasing the β value in *p*-nitroaniline, **1**, and suggests that H bonding should be considered in all cases in which it can occur.

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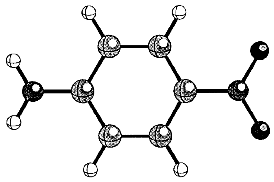
* Fax: +34-64-345747; E-mail: eperis@vents.uji.es

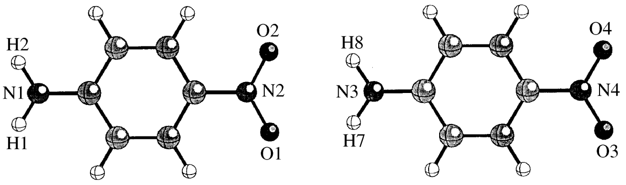
Results and Discussion

Hydrogen bonding in *p*-nitroaniline and HF clusters

We first consider the case represented by two monomers of *p*-nitroaniline, **1**, brought together by means of hydrogen bonding. Fig. 1 shows the completely optimized structure of this dimer, assumed to be the global minimum of the potential energy surfaces, with the atom numbering. Table 1 shows the most important geometric parameters of the *p*-nitroaniline dimer $(\mathbf{1})_2$. The distances and angles obtained for the monomer are very similar to those obtained previously by other theoretical procedures.[5b] Our calculations have been based on a planar geometry of the molecules, characterizing a head-to-tail structure with two H bond interactions. Some other features may be pointed out. The H bond distances (O1—H7 or O2—H8) increase when diffuse and polarization functions are included in the basis set. The same effect is observed at the MP2 and B3LYP levels if compared with the Hartree–Fock results. It is important to note that H bond interactions induce a slight reduction of the H7—N3—H8 and O1—N2—O2 angles from the angles in the monomer. Thus, these values are smaller than those not showing H bonding, *i.e.*, H1—N1—H2 and O3—N4—O4, respectively, at all levels of calculation. The HF optimizations with the applied electric field give similar trends due to the electronic interactions with the electric field. The computational results can be compared with experimental data showing the improvement obtained when correlation energy is considered.[3c]



p-Nitroaniline monomer, **1**



p-Nitroaniline dimer, $(\mathbf{1})_2$

Fig. 1 Optimized structures of the monomer and dimer of *p*-nitroaniline obtained from HF/6-31+G** calculations

Absolute and H bond energies, dipole moments and hyperpolarizabilities of *p*-nitroaniline **1** and the H-bonded dimer $(\mathbf{1})_2$ are listed in Table 2. Analysis of the results shows that the H bond strength in this dimer is in the range of 2.5–5.7 kcal mol^{-1} per hydrogen bond, depending on the level of calculation used; since each dimer has two of these bonds the dissociation energy for the dimer is in the range of 5–11.4 kcal dimer^{-1}. The crystal structure of **1** shows that only one H bond is formed between each pair of $NH_2—NO_2$ fragments, in such a way that only one N—H bond is connected by a bifurcated H bond to both oxygen atoms of the NO_2 fragment.[3d] This kind of arrangement may be due to packing forces that we have not considered in our calculations and in fact, we assume that it corresponds to a local minimum of higher energy than the one we characterize. Some other nitroanilines[3d] show two H bonds between consecutive $NH_2—NO_2$ groups, similar to our optimized geometry for $(\mathbf{1})_2$ (Fig. 1). Etter and colleagues[3d] reported two N—H stretching frequencies for the solid state IR spectrum of **1**: 3570 cm^{-1}(s) and 3450 cm^{-1}(w). These values can be calculated if a frequency analysis is carried out. In this sense, the calculated IR-active stretching frequency for the free N—H obtained at the B3LYP level is 3607 cm^{-1} while the H-bonded N—H one is 3552 cm^{-1}, in great agreement with the reported experimental data.[3d] Iogansen[8] has reported a very useful equation to estimate the H-bond strength from IR data, which we have used to estimate the H bond strength in compound $(\mathbf{1})_2$ at 3.4 kcal mol^{-1}, from the experimental stretching frequencies of 3570 cm^{-1} (free N—H) and 3450 cm^{-1} (H-

Table 1 Geometrical parameters (distances in Å, angles in degrees) of H-bonded *p*-nitroaniline dimer $(\mathbf{1})_2$. Hartree–Fock results obtained with and without a 0.005 a.u. electric dipole field applied opposite to the dipole moment direction

	EDF = 0				EDF = 0.005 a.u		
	HF/6-31G	HF/6-31+G**	B3LYP/6-31G	B3LYP/6-31+G**	MP2/6-31G	HF/6-31G	HF/6-31+G**
O1—H7	2.407	2.513	2.258	2.367	2.346	2.295	2.389
H1—N1—H2	117.47	117.78	117.58	117.56	117.59	116.74	117.19
H7—N3—H8	115.18	115.88	114.11	114.69	114.88	113.64	114.60
O3—N4—O4	122.64	123.90	122.92	123.50	123.06	121.51	122.76
O1—N2—O2	122.31	123.54	122.61	123.14	122.95	121.02	122.28
H8—O2—N2	113.04	113.29	111.77	112.56	111.69	113.26	113.59
N3—H8—O2	128.21	127.00	129.87	128.53	129.39	129.41	127.97

Table 2 Hydrogen bond energy (kcal mol^{-1}), dipole moment (μ in D) and hyperpolarizability (β in 10^{-30} esu) of *p*-nitroaniline **1** and the H-bonded dimer $(\mathbf{1})_2$. Hartree–Fock results obtained with a 0.005 a.u. electric dipole field applied

	Experimental	HF/6-31G		HF/6-31+G**		B3LYP/6-31G		B3LYP/6-31+G**		MP2/6-31G	
		1	$(\mathbf{1})_2$	**1**	$(\mathbf{1})_2$	**1**	$(\mathbf{1})_2$	**1**	$(\mathbf{1})_2$	**1**	$(\mathbf{1})_2$
H bond energy		—	5.69	—	4.41	—	4.99	—	3.36	—	2.54
β_{zzz}		11.70	41.40	9.79	32.27						
β_{zxx}		−0.04	−0.09	−0.35	−0.64						
β_{zyy}		−1.98	−4.67	−1.73	−3.94						
β	27.6[b], 28.8[c], 35.4[c], 36.0[d]	9.68	36.64	7.71	27.62						
μ	6.3[a]	8.50	20.08	7.84	22.11	7.69	19.22	7.93	18.76	6.71	16.24

[a] μ obtained from ref. 24. [b–d] β values obtained from [b] ref. 5c (in acetone), [c] ref. 5d (in 1,4-dioxane) and [d] ref. 5e (in DMSO). Absolute energy/hartrees of **1**: HF/6-31G = −489.011432, HF/6-31+G** = −489.254294, B3LYP/6-31G = −491.964762, B3LYP/6-31+G** = −492.145473, MP2/6-31G = −490.020811.

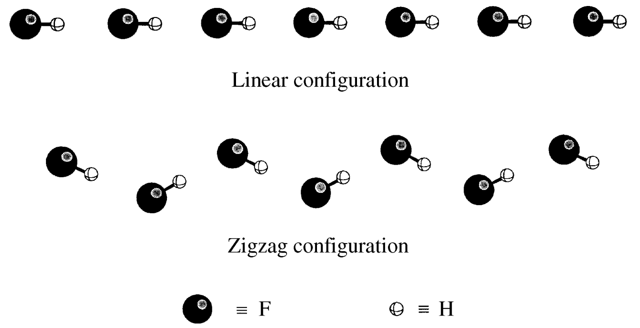


Fig. 2 Optimized structures of the linear and zigzag configurations for the $(HF)_7$ chain obtained from HF/6-31+G** calculations

bonded N—H). This value falls within the range of our calculated data.

Basis set superposition errors (BSSE) have been estimated by computation of counterpoise corrections,[9] but because of the tendency of this correction to overestimate the BSSE[10] we finally decided not to include them.

The calculated dipole moments of the monomer and the dimer reflect the degree of charge-transfer interaction in the ground state. As expected, the dipole moment increases from monomer to dimer. The MP2 values are closer to the experimental data than those obtained with B3LYP or Hartree–Fock (see Table 2).

In order to judge the effect of H bonding on the value of the hyperpolarizability β, we have studied the simplest system for which this type of interaction can be calculated. Hydrogen fluoride is a well known system in which the H bond is so strong that even in the gas phase chains of up to seven molecules can be present. Although it was originally thought that the system consisted of cyclic hexamers in the gas phase,[11a] the latest theories support the idea of short linear chains. The simplicity of the molecule and the presence of a (head-to-tail) H bond type makes this system optimum for theoretical calculations. We have obtained an optimized geometry in which the HF molecules show a linear disposition with FHF angles of 180°, and also a zigzag chain structure as seen in the crystal structure of HF,[11b] with H···F—H angles in the range of 130–154° and 120–122° with the Hartree–Fock and MP2 methods, respectively. Fig. 2 shows the two optimized structures that we obtained. Table 3 and 4 give the most relevant geometric parameters for systems of chains of up to seven molecules. From a geometrical point of view, MP2 seems to be more appropriate than Hartree–Fock to describe this kind of system: the H···F—H and F—H···F angles are closer to the experimental results. Energies, dipole moments and hyperpolarizabilities are listed in Table 5. In both arrangements, the calculated H bond energies fall close to the experimental value of 6.6 kcal mol^{-1}. It is noteworthy that there is a linear dependence of the dipole moment μ on increasing nuclearity in the linear HF clusters (Table 5).

NLO properties of *p*-nitroaniline and HF clusters

From the calculated structures discussed above for *p*-nitroaniline, we theoretically calculated the NLO properties of this system. We thought that some contribution might arise from the H-bonded dimer and that this could have been one of the main reasons for the disparities between the prior theoretical values and the experimental data. We also calculated β for HF clusters, in order to study the effect of H bonding in head-to-tail aggregates on the NLO properties of the system.

The calculations of β were performed using HF/631-G and HF/631 + G** methods with the program Gaussian94. An external field of 0.005 a.u., oriented opposite to the dipole moment of the molecule, was applied. Although inclusion of the correlation energy may improve calculated NLO properties, MP2 and B3LYP methods failed to give β values when the external field was applied.

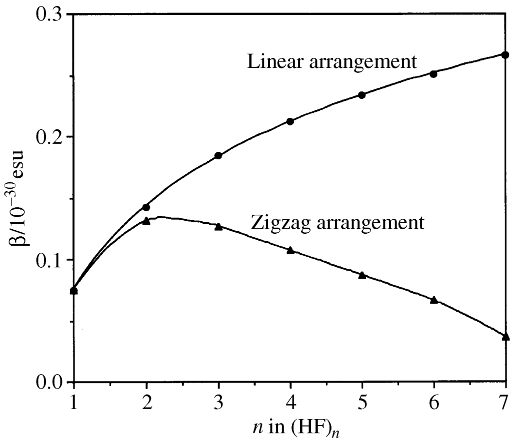


Fig. 3 Representation of the theoretical value of β as a function of n in $(HF)_n$. Results are obtained from HF/6-31+G** calculations with a 0.005 a.u. electric dipole field

The theoretical values of β for the monomer of *p*-nitroaniline, **1**, obtained at the HF level of theory with a extended basis set (Table 2) are in agreement with experimental data.[5b] These theoretical values, which are directly comparable to experimental ones determined in the gas phase, are consistently three times smaller than those extracted from solution phase measurements.

When we consider the formation of the dimer $(\mathbf{1})_2$, a clear increase in the value of β is observed. This value is also associated with a large increase in the value of the dipole moment μ. In fact, these data are very close to those obtained from experimental methods[5c–e] after multiplying these by a factor of three, according to the new interpretation of the experimental data.[5b]

For HF clusters, a clear dependence of the theoretical value of β is observed when we increase the number of molecules in the system. Furthermore, there is a large change in this parameter when we go from the linear arrangement to the zigzag geometry. In the zigzag geometry there is a progressive decrease in β as we increase n in $(HF)_n$. The opposite effect is observed for the linear structure, where a linear dependence of β on n is observed. In both cases the value of the dipole moment μ increases with the number of molecules in the cluster. We assign this difference of behaviour in both systems to the larger charge transfer possibilities in the linear arrangement of the cluster, which has a pseudo-*trans* linear geometry of the two H ligands (one covalent, another H-bonded) that share the same $F(p_z)$ orbitals. Fig. 3 shows both trends.

Computational Details

In vacuo calculations were performed with the Gaussian94 package of programs.[12] *Ab initio* molecular orbital calculations were performed at the Hartree–Fock level with 6-31G and 6-31 + G** basis sets. Electron correlation was taken into account by using the second-order Møller–Plesset perturbation (MP2) method.[13] Because the experimental determination of the hyperpolarizability of *p*-nitroaniline is always carried out in solution using the traditional EFISH method,[5] in which a strong static field is applied to a solution of the chromophore, we used an electron field of 0.005 a.u., opposite to the permanent dipole of the molecule, to simulate the experimental conditions under which the measurements of β are carried out.

A molecule in an applied electric field exhibits an induced

Table 3 Geometrical parameters (distances in Å, angles in degrees) of $(HF)_n$ clusters. Parameters obtained by means of the HF/6-31+G** method with a 0.005 electric dipole field applied

Linear arrangement								
$(HF)_n$	$n =$	1	2	3	4	5	6	7
F—H		0.904	0.907	0.909	0.909	0.910	0.910	0.910
			0.906	0.911	0.913	0.914	0.914	0.915
				0.907	0.912	0.915	0.916	0.916
					0.907	0.913	0.915	0.917
						0.907	0.913	0.916
							0.907	0.913
								0.907
F···H			1.952	1.888	1.864	1.862	1.853	1.851
				1.867	1.797	1.776	1.766	1.762
					1.844	1.767	1.747	1.736
						1.830	1.759	1.734
							1.826	1.753
Zigzag arrangement								
$(HF)_n$	$n =$	1	2	3	4	5	6	7
F—H		0.915	0.908	0.910	0.911	0.911	0.911	0.911
			0.906	0.912	0.916	0.917	0.918	0.918
				0.907	0.914	0.918	0.920	0.921
					0.908	0.915	0.920	0.921
						0.908	0.916	0.920
							0.908	0.916
								0.908
F···H			1.927	1.846	1.827	1.815	1.813	1.813
				1.821	1.745	1.721	1.709	1.704
					1.796	1.718	1.690	1.678
						1.778	1.701	1.675
							1.772	1.695
								1.769
F—H···F			172.3	173.0	172.7	172.6	172.6	172.1
				179.5	179.4	178.9	178.7	178.3
					176.7	177.1	176.6	176.4
						177.0	177.4	176.5
							176.3	177.3
								176.5
H···F—H			154.0	144.5	146.3	145.0	145.4	145.6
				137.6	132.0	131.4	130.9	131.5
					140.6	134.4	133.8	133.2
						139.6	133.4	133.4
							140.5	133.9
								140.3

F—H = bond distance. F···H = hydrogen bond distance.

dipole moment. This induced moment can be expanded in a Taylor series in powers of the applied electric field (F) as shown in eq. 1,

$$\mu_i(F) = \mu_i(0) + \sum_j \alpha_{ij} F_j + \sum_{jk} \beta_{ijk} F_j F_k \sum_{jkl} \gamma_{ijkl} F_j F_k F_l + \cdots \tag{1}$$

where $\mu_i(0)$ is its permanent dipole moment, α_{ij} is the dipole polarizability, and β_{ijk} and γ_{ijkl} are the first and second hyperpolarizabilities, respectively. The theoretical values of the hyperpolarizability tensors may be compared with the experimental data when β_i is defined as $\beta_i = \sum_j \beta_{ijj}$, so that β_z would be $\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$, where z is the axis of the dipole moment, and finally $\beta = (\beta_x{}^2 + \beta_x{}^2 + \beta_z{}^2)^{\frac{1}{2}}$.

We also employed methods based on DFT,[14,15,16] with the Becke 3 parameter functional (B3)[17] and the correlation functional of Lee, Yang and Parr (LYP).[18] The parameters are those determined by Becke by fitting to the G1[19] molecule set.[17b,20]

The geometries of $(HF)_n$ clusters, for $n = 1$ to 7, and the monomer and dimer of *p*-nitroaniline have been completely optimized *in vacuo*. Using the Gaussian94, Hartree–Fock optimizations were also carried out with a 0.005 a.u. electric dipole field (EDF) in order to determine whether the structures would change.

The requested convergence on the density matrix was 10^{-9} a.u.; the threshold value of the maximum displacement was 0.0018 Å and that of the maximum force was 0.00045 hartree/bohr using the Berny analytical gradient optimization routine.[21,22] The nature of the stationary point was checked by diagonalizing the Hessian matrix to determine the number of imaginary frequencies[23] (zero for local minima).

Conclusions

By using the program Gaussian94 we have applied a finite field approach to the calculation of second-order hyperpolarizability coefficients, which are readily obtained. It is found that the theoretical values obtained are in excellent agreement with those reported previously when a monomer is considered, but that the values are three times lower than the experimental ones. We have considered the possibility that the formation of H-bonded dimers of *p*-nitroaniline is responsible and we have studied this in detail. Geometries and association energies have been estimated and have been related to the available experimental data. We find that the β values obtained by the same methodology are close to the experimental ones. In order to see if the effect of H bonding on the second-order hyperpolarizability coefficients also applies to other systems, we studied a system in which H bonding is well-known, HF, where we find a clear dependence of β on the

Table 4 Geometrical parameters (distances in Å, angles in degrees) of $(HF)_n$ clusters. Parameters obtained by means of the MP2/6-31+G** method

Linear arrangement							
$(FH)_n$	$n =$	1	2	3	4	5	6
F—H		0.926	0.929 0.927	0.931 0.932 0.928	0.931 0.934 0.933 0.928	0.932 0.935 0.936 0.934 0.929	0.932 0.936 0.937 0.937 0.934 0.929
F···H			1.937	1.869 1.844	1.844 1.770 1.820	1.837 1.748 1.741 1.804	1.832 1.737 1.715 1.728 1.799
Zigzag arrangement							
$(FH)_n$	$n =$	1	2	3	4	5	6
F—H		0.926	0.932 0.929	0.934 0.938 0.930	0.935 0.941 0.940 0.931	0.936 0.944 0.945 0.941 0.931	0.936 0.945 0.948 0.947 0.942 0.931
F···H			1.850	1.788 1.758	1.766 1.693 1.731	1.755 1.662 1.654 1.714	1.748 1.648 1.624 1.637 1.707
F—H···F			169.70	175.85 175.26	177.00 178.03 176.40	178.40 178.01 178.61 177.46	178.77 179.84 179.20 179.51 178.22
H···F—H			119.50	121.20 123.59	120.55 122.86 124.02	121.45 121.71 122.64 124.56	121.11 122.20 121.74 123.13 124.92

F—H = bond distance. F···H = hydrogen bond distance.

chain length of the aggregates. A clear increase in β is observed for linear chains of HF, while a decrease of the nonlinear coefficient is seen for the zigzag arrangement. In typical NLO materials a significant enhancement of β has been found to result from extending the length of the conjugated covalent chain connecting the donor and acceptor groups. We have now shown that connecting molecules *via* intermolecular hydrogen bonding, especially when this gives rise to a linear and monodimensional structure, must be considered as a useful second way of linking donor and acceptor. Hydrogen bonding helps increase the chain length between donor and acceptor, and provides an appropriate pathway for intermolecular charge transfer leading to a significant net enhancement of the NLO properties of the system. Since hydrogen bonding can be conveniently controlled by incorporating appropriate H bond donor and acceptor groups, this provides a powerful new strategy to enhance the NLO properties of molecules that are already NLO-active.

According to our calculations we can conclude that there is some contribution of the dimer to the experimental measurements of the second-order hyperpolarizability coefficients in *p*-nitroaniline.

Table 5 Hydrogen bond energy (kcal mol^{-1}), dipole moment (μ in D) and hyperpolarizability (β in 10^{-30} esu) of $(HF)_n$ clusters. Hartree–Fock results obtained with a 0.005 a.u. electric dipole field applied

	Hydrogen bond energy				μ				β	
	Linear		Zigzag		Linear		Zigzag		Linear	Zigzag
n	HF/6-31 +G**	MP2/6-31 +G**	HF/6-31 +G**	MP2/6-31 +G**	HF/6-31 +G**	MP2/6-31 +G**	HF/6-31 +G**	MP2/6-31 +G**	HF/6-31 +G**	HF/6-31 +G**
1	—	—	—	—	2.04	2.02	2.04	2.02	0.075	0.075
2	4.15	4.14	4.21	4.03	4.42	4.40	4.36	3.77	0.1427	0.131
3	4.85	4.87	5.09	5.01	6.93	6.95	6.67	6.38	0.1841	0.127
4	5.28	5.31	5.61	5.61	9.52	9.58	9.17	8.77	0.2125	0.107
5	5.56	5.61	5.96	6.01	12.15	12.27	11.67	11.45	0.2340	0.087
6	5.76	5.82	6.20	6.30	14.80	14.99	14.24	14.01	0.2510	0.066
7	5.89		6.38		17.46		16.82		0.2657	0.036

Absolute energy/hartrees of HF ($n = 1$): HF/6-31+G** = −100.028382 and MP2/6-31G** = −100.218904.

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