Ab Initio and DFT Calculations on 2-Aminopyrimidine, 2-Amino-4,6-dichloropyrimidine, and Their Dimers

Ahmed Abd El-gawad Hasanein* and Samir Abd El-aziz Senior

Department of Chemistry, Faculty of Science, Alexandria University,
P. O. Box 426, Ibrahemia, 21321, Alexandria, Egypt

Received July 11, 2006; E-mail: aahasanein@yahoo.com

Optimum molecular geometries of 2-aminopyrimidine and 2-amino-4,6-dichloropyrimidine have been calculated by using MP2 and B3LYP methods with different extended basis sets. Dimer interactions for these two pyrimidine derivatives have been also investigated. Full geometry optimization at MP2 and B3LYP levels has been performed for the dimers. BSSE correction was made using the counterpoise method, and the H-bond energies have been calculated.

The different electronic properties of nucleic acid bases and their derivatives are very important for understanding many structural aspects of DNA. Many of the nucleic acid bases and their intermolecular complexes have been the subject of extensive experimental studies[1–10] as well as theoretical calculations of their electronic properties.[11–14] Ab initio calculations at the HF/6-31G** level have been performed on dihydroxypyrimidinone, uracil, thymine, and other nucleic acid bases.[15] The nonrigidity of the pyrimidine ring has been discussed. The interaction between two different pyrimidine bases and even triplexes has been also investigated theoretically at various levels of theory.[16–36] Molecular geometries, tautomerism and other one electron properties have been calculated.

In the present work, theoretical calculations using several state-of-the art methods on 2-aminopyrimidine (I) and 2-amino-4,6-dichloropyrimidine (II) and some of their possible intermolecular dimer interactions have been performed. Optimum molecular geometries of monomers and dimers, H-bond interaction energies with BSSE correction, electron density distributions, amount of charge transferred, and site of electron donation upon dimer formation have been investigated.

Methods of Calculations

Ab initio as well as density functional theory have proven to be very powerful tools for obtaining optimum molecular geometries and calculating other molecular electronic properties. We performed, here, ab initio and B3LYP[37] calculations[#] on I, II and their dimer interactions using the Gaussian 94 package.[38] The default parameters of the G94 program were used in all computations. The MP2 computations were performed using the frozen core (FC) option where the correlation energy calculations were excluded for the core electrons. The FC option in MP2 calculations substantially saves CPU time at the expense of a small difference in the optimized geometries and energies. The molecular geometries of I, II and their dimers were fully optimized in the gas phase. The basis sets used were 6-31+G, 6-31++G, 6-31+G**, 6-31++G**, and 6-311++G**. The basis set superposition error (BSSE) was estimated using the counterpoise method.[39,40]

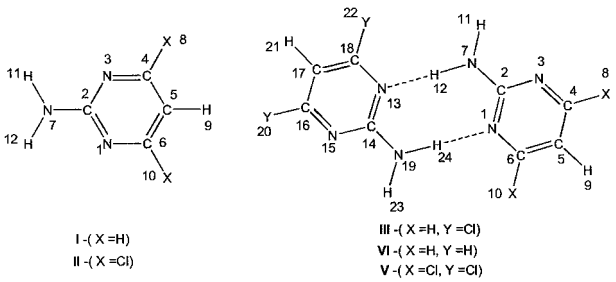

Fig. 1. The numbering Schemes for 2-aminopyrimidine (I), 2-amino-4,6-dichloropyrimidine (II), and their dimers (III, IV, and V).

Results and Discussion

The numbering of atoms adopted for 2-aminopyrimidine (I), 2-amino-4,6-dichloropyrimidine (II), and their dimers (III, IV, and V) are shown in Fig. 1. The optimum molecular geometry of compounds I and II calculated through a full geometry optimization by the MP2 and B3LYP methods and using different extended basis sets are given in Tables 1 and 2.

Monomers. MP2 Calculations: The MP2 calculated bond lengths (*r*), bond angles (*a*), and dihedral angles (*d*) of compounds I and II (Table 1) are affected by the size of basis set used in the calculations and show some general trends. The *r* of the C(2)–N(1) and C(2)–N(3) bonds decreased as the size of the basis set increased in the order 6-31+G, 6-31++G, 6-31+G**, 6-31++G**, and 6-311++G**. Their calculated values are in the range of 1.346–1.375 Å for compound I and 1.347–1.377 Å for compound II. The average value of these two bond lengths from X-ray data is 1.32 Å for II, 4-amino-2,6-dichloropyrimidine, and 2-amino-6-chloro-4-methylpyrimidine.[41–43] The same is true for *r* of the C(6)–N(1) and C(4)–N(3) bonds. Their calculated values are in the range of 1.326–1.367 Å for compound I and 1.326–1.344 Å for compound II. Their average value from X-ray data is 1.30 Å.[41–43] On the other hand, the *r* for the C(2)–N(7) bond was found to increase as the size of the basis set increased. Its calculated values are in the range 1.375–1.377 Å for compound I and

Published on the web February 13, 2007; doi:10.1246/bcsj.80.307

Table 1. MP2 Optimum Geometries for Compounds I and II Using Different Extended Basis Sets

		MP2									
		6-31+G		6-31++G		6-31+G**		6-31++G**		6-311++G**	
		I	II	I	II	I	II	I	II	I	II
r[a)]	1-2	1.3755	1.3769	1.3755	1.3768	1.3493	1.3499	1.3494	1.3498	1.3465	1.3471
	1-6	1.3673	1.3445	1.3672	1.3444	1.3411	1.3286	1.3412	1.3288	1.3384	1.3257
	2-3	1.3758	1.3769	1.3755	1.3767	1.3495	1.3497	1.3496	1.3498	1.3465	1.3471
	2-7	1.3752	1.3644	1.3754	1.3642	1.3754	1.3663	1.3755	1.3664	1.3768	1.3675
	3-4	1.3672	1.3445	1.3672	1.3444	1.3411	1.3288	1.3411	1.3288	1.3384	1.3257
	4-5	1.4099	1.4055	1.4098	1.4054	1.3938	1.3936	1.3938	1.3936	1.3953	1.3947
	4-8	1.0887	1.8232	1.0886	1.8234	1.0841	1.7310	1.0841	1.7310	1.0882	1.7288
	5-6	1.4099	1.4056	1.4098	1.4055	1.3938	1.3937	1.3938	1.3936	1.3953	1.3947
	5-9	1.0893	1.0863	1.0893	1.0862	1.0805	1.0785	1.0805	1.0785	1.0837	1.0816
	6-10	1.0886	1.8233	1.0886	1.8235	1.0841	1.7311	1.0841	1.7310	1.0882	1.7288
	7-11	1.0113	1.0113	1.0114	1.0113	1.0083	1.0081	1.0084	1.0080	1.0094	1.009
	7-12	1.0113	1.0113	1.0114	1.0113	1.0084	1.0081	1.0083	1.0080	1.0094	1.009
a[a)]	2-1-6	116.270	115.905	116.265	115.909	115.745	115.331	115.742	115.333	115.731	115.317
	1-2-3	125.665	124.865	125.662	124.864	126.660	126.467	126.660	126.469	126.838	126.634
	1-2-7	117.168	117.566	117.162	117.566	116.641	116.730	116.653	116.734	116.548	116.652
	2-3-4	116.257	115.905	116.264	115.909	115.741	115.335	115.735	115.334	115.732	115.317
	3-4-5	122.394	124.452	122.388	124.446	122.750	124.183	122.757	124.182	122.748	124.173
	3-4-8	115.632	116.477	115.608	116.476	115.838	116.594	115.829	116.591	115.987	116.740
	4-5-6	117.028	114.421	117.025	114.424	116.343	114.486	116.342	114.487	116.186	114.370
	4-5-9	121.482	122.787	121.487	122.784	121.828	122.760	121.825	122.754	121.904	122.812
	1-6-5	122.384	124.452	122.388	124.446	122.750	124.188	122.749	124.183	122.748	124.173
	1-6-10	115.632	116.480	115.609	116.478	115.843	116.602	115.829	116.591	115.987	116.740
	2-7-12	118.827	119.685	118.726	119.681	115.328	116.277	115.312	116.250	114.879	115.810
	11-7-12	119.955	120.627	119.863	120.634	116.265	117.292	116.240	117.306	116.019	117.165
d[a)]	7-2-1-6	178.093	179.923	177.906	179.914	175.981	176.202	175.980	176.151	175.78	175.948
	7-2-3-4	178.079	179.928	177.907	179.920	175.983	176.169	175.967	176.140	175.780	175.949
	11-7-2-1	171.914	179.782	171.412	179.738	161.338	163.661	161.279	163.603	160.564	162.763
	11-7-2-3	9.489	0.263	9.994	0.313	21.3822	19.025	21.421	19.100	22.142	19.900
	12-7-2-1	9.453	0.271	9.989	0.321	21.3578	19.193	21.425	19.187	22.140	19.893
	12-7-2-3	171.950	179.774	171.417	179.730	161.362	163.492	161.275	163.515	160.566	162.770
	1-2-3-4	0.385	0.024	0.553	0.025	0.986	0.848	1.025	0.859	1.195	0.311
	2-3-4-5	0.108	0.006	0.133	0.008	0.001	0.082	0.022	0.103	0.041	0.449
	3-4-5-6	0.558	0.027	0.737	0.031	0.840	0.889	0.925	0.916	0.933	0.236
	6-5-4-8	179.468	179.969	179.305	179.965	179.022	179.116	178.973	179.039	178.855	179.779

a) r (Å), a (degree), d (degree).

1.364–1.367 Å for compound II. These ranges show a reasonable agreement with the value determined from X-ray analysis (1.34 Å).[43,44] This indicates that the C(6)–N(1) and C(4)–N(3) bonds have higher double bond character than the C(2)–N(1) and C(2)–N(3) bonds. This may be attributed to the presence of the NH_2 group that is attached to C(2), where r for the C(2)–N(7) bond is calculated to be the longest. The r value for the C(5)–C(4) and C(5)–C(6) bonds of I (1.395–1.410 Å) and II (1.395–1.406 Å) slightly decreased as the size of the basis set increased. These ranges show the double bond character of these two bonds. These two r values are similar to that determined from X-ray data (1.40 Å).[41–43] In addition, r_{C-H} and r_{N-H} slightly decrease as the size of the basis set increased. The calculated r_{C-H} values are in the range of 1.084–1.089 Å for compound I and 1.082–1.086 Å for compound II, and for the r_{N-H} values are in the range of 1.009–1.011 Å for compound I and 1.008–1.011 Å for compound II. The values of r_{C-Cl} were calculated to be in the range of 1.729–1.823 Å for compound II, and they decreased as the basis set size was increased. This range is consistent with that from X-ray data (1.77–1.78 Å).[41–43] From the above comparison between the calculated and experimental bond distances, the best agreement is obtained by using the 6-311++G** basis set.

The calculated a for the angle N(1)–C(2)–N(3) slightly increased as the size of the basis set is increased: about 1° for compound I and 2° for compound II. All other values showed a very slight decrease, and the pyrimidine ring showed no deviation from planarity either for compound I or compound II. The calculated a values for the N–C–N, C–N–C, N–C–C, and C–C–C ring bond angles using the different extended basis sets were found to be in the ranges 125.66–126.84, 115.73–116.27, 122.38–122.75, and 116.19–117.03°, respectively, for compound I. The calculated ranges for these bond angles in compound II are found to be 124.86–126.63, 115.32–115.90, 124.17–124.45, and 114.37–114.42°, respectively. These values show that the ring is not a perfect hexagon; however, assuming a strictly planar structure, they show that the pyrimidine ring is aromatic. The X-ray data[41,42] gave values for these

Table 2. B3LYP Optimum Geometries for Compounds I and II Using Different Extended Basis Sets

		B3LYP									
		6-31+G		6-31++G		6-31+G**		6-31++G**		6-311++G**	
		I	II	I	II	I	II	I	II	I	II
r[a)]	1-2	1.3625	1.3625	1.3625	1.3624	1.3495	1.3498	1.3495	1.3500	1.3461	1.3468
	1-6	1.3476	1.3240	1.3476	1.3239	1.3342	1.3187	1.3343	1.3188	1.3307	1.3145
	2-3	1.3622	1.3623	1.3623	1.3622	1.3494	1.3497	1.3495	1.3496	1.3461	1.3467
	2-7	1.3601	1.3525	1.3601	1.3525	1.3642	1.3538	1.3642	1.3540	1.3629	1.3523
	3-4	1.3478	1.3240	1.3478	1.3239	1.3342	1.3188	1.3342	1.3189	1.3307	1.3146
	4-5	1.4001	1.3974	1.4001	1.3974	1.3958	1.396	1.3959	1.3962	1.3924	1.3926
	4-8	1.0849	1.8137	1.0848	1.8138	1.0886	1.7522	1.0885	1.7520	1.0870	1.7528
	5-6	1.4001	1.3975	1.4001	1.3974	1.3957	1.3961	1.3957	1.3961	1.3924	1.3926
	5-9	1.0828	1.0788	1.0828	1.0787	1.0835	1.0799	1.0835	1.0798	1.0815	1.0778
	6-10	1.0849	1.8139	1.0849	1.8139	1.0886	1.7521	1.0885	1.7525	1.0870	1.7528
	7-11	1.0067	1.0073	1.0067	1.0073	1.0075	1.0068	1.0075	1.0068	1.0060	1.0053
	7-12	1.0067	1.0073	1.0067	1.0073	1.0075	1.0068	1.0075	1.0068	1.0060	1.0053
a[a)]	2-1-6	116.604	116.541	116.597	116.545	115.919	115.625	115.910	115.615	115.977	115.706
	1-2-3	125.198	124.038	125.204	124.035	126.316	125.867	126.323	125.855	126.253	125.721
	1-2-7	117.394	117.976	117.391	117.977	116.834	117.064	116.840	117.059	116.870	117.138
	2-3-4	116.616	116.551	116.609	116.554	115.921	115.62	115.920	115.644	115.977	115.707
	3-4-5	122.508	124.584	122.511	124.583	123.002	124.603	122.999	124.596	122.963	124.609
	3-4-8	115.853	116.713	115.849	116.714	115.934	116.632	115.938	116.632	116.014	116.666
	4-5-6	116.551	113.695	116.553	113.693	115.832	113.682	115.833	113.668	115.863	113.646
	4-5-9	121.718	123.146	121.717	123.147	122.083	123.164	122.073	123.153	122.068	123.178
	1-6-5	122.524	124.591	122.527	124.589	123.005	124.601	123.009	124.622	122.962	124.610
	1-6-10	115.863	116.710	115.860	116.713	115.933	116.636	115.930	116.621	116.013	116.667
	2-7-12	119.560	119.649	119.566	119.657	118.157	119.569	118.180	119.569	118.122	119.552
	11-7-12	120.874	120.700	120.861	120.681	119.384	120.856	119.372	120.843	119.384	120.890
d[a)]	7-2-1-6	179.963	179.997	179.966	179.998	178.051	179.905	178.057	179.867	178.158	179.995
	7-2-3-4	179.957	179.988	179.959	179.989	178.054	179.880	178.056	179.872	178.158	179.998
	11-7-2-1	179.938	179.998	179.940	179.999	168.905	179.600	168.900	179.683	168.699	179.586
	11-7-2-3	0.020	0.017	0.021	0.016	12.272	0.495	12.212	0.430	12.289	0.372
	12-7-2-1	0.065	0.008	0.062	0.009	12.288	0.516	12.247	0.447	12.290	0.372
	12-7-2-3	179.977	179.973	179.977	179.975	168.890	179.579	168.865	179.667	168.697	179.586
	1-2-3-4	0.003	0.007	0.001	0.007	0.642	0.016	0.712	0.004	0.750	0.049
	2-3-4-5	0.006	0.007	0.006	0.007	0.108	0.021	0.136	0.015	0.145	0.000
	3-4-5-6	0.007	0.011	0.006	0.011	0.339	0.003	0.350	0.028	0.366	0.039
	6-5-4-8	179.994	179.990	179.994	179.990	179.507	179.966	179.479	179.952	179.489	179.998

a) r (Å), a (degree), d (degree).

bond angles of 128, 114, 125.5, and 113°, respectively, which are in reasonable agreement with the MP2 calculated a values especially using the 6-311++G** basis set.

From the calculated d values for H(11)–N(7)–C(2)–N(3) and H(12)–N(7)–C(2)–N(1) for compound I, the HNH plane of the amino group makes an angle with the ring with an average value of 9.471 and 9.992° using the 6-31+G and 6-31++G basis sets, respectively, and an average value of 21.370, 21.423, and 22.141° using the 6-31+G**, 6-31++G**, and 6-311++G** basis sets, respectively. For compound II, these average values are 0.267 and 0.317° using the 6-31+G and 6-31++G basis sets, respectively, and 19.109, 19.144, and 19.897°, respectively. This indicates that if the cartesian gaussian polarization functions are not used in the calculations, the amino group is predicted to be nearly planar with the pyrimidine ring, especially for compound II. It is worth noting that the largest values for these two dihedral angles are obtained using the 6-311++G** basis sets: 22.141° for compound I and 19.897° for compound II. This indicates that the MP2/6-311++G** predicted that the amino group adopts a nearly pyramidal (non planar) geometry, as expected.

B3LYP Calculations: Table 2 summarizes the B3LYP optimum molecular geometries of compounds I and II using different extended basis sets. The calculated r, a, and d values are also affected by the size of the basis set used and show more or less the same general trends obtained by MP2 calculations. The r for the C(2)–N(1) and C(2)–N(3) bonds slightly decreased as the size of the basis set used was increased in the order 6-31+G, 6-31++G, 6-31+G**, 6-31++G**, and 6-311++G**. The calculated values are in the range of 1.346–1.362 Å for compound I and 1.347–1.362 Å for compound II. The r values for the C(6)–N(1) and C(4)–N(3) bonds were also found to decrease. The calculated values are in the range of 1.331–1.348 Å for compound I and 1.314–1.324 Å for compound II. The r values of the C(2)–N(7) bond was found to increase slightly as the size of the basis set increase. Its calculated values are found to be in the range of 1.360–1.363 Å for compound I and 1.352–1.354 Å for compound II. The B3LYP

results also indicate that the C(6)–N(1) and C(4)–N(3) bonds have the highest double bond character, and the C–NH_2 bond is the longest, which indicates that it has sp^3 hybridization. The r_{C-C} values (I, 1.392–1.400 Å; II, 1.393–1.397 Å) are only slightly affected by the size of the basis set. The calculated r_{C-H} values are in the range of 1.082–1.087 Å for compound I and 1.078–1.079 Å for compound II. The values of r_{N-H} are in the range of 1.006–1.007 Å for compound I and 1.005–1.007 Å for compound II, showing almost no effect upon increasing the size of the basis set used. The r_{C-Cl} values (1.753–1.814 Å for compound II) decreased as the basis set size was increased. All of the above mentioned B3LYP calculated ranges of *r* are in good agreement with those from X-ray data[41–44] especially using the 6-311++G** basis set.

The calculated *a* values for the angle N(1)–C(2)–N(3) had an increase of approximately 2° as the size of the basis set increased. All other ring *a* values are either unaffected or slightly affected by the size of the basis set used. The pyrimidine ring showed no deviation from planarity either for compound I or compound II. The calculated *a* values for the ring angles N–C–N, C–N–C, N–C–C, and C–C–C using different extended basis sets are found to be in the ranges 125.20–126.25, 115.98–116.62, 122.51–122.96, and 115.86–116.55°, respectively, for compound I, and for compound II, they were 124.04–125.72, 115.71–116.55, 124.58–124.61, and 113.65–113.69°, respectively. These B3LYP calculated values are in good agreement with those from X-ray data (128, 114, 125.5, and 113°, respectively).[41,42] This indicates that the pyrimidine ring assumes a somewhat deformed but strictly planar hexagon. As well, the B3LYP as well as the MP2 methods confirm the aromaticity of the pyrimidine ring.

The calculated *d* values for H(11)–N(7)–C(2)–N(3) and H(12)–N(7)–C(2)–N(1) show that the HNH plane of the amino group makes an angle with the pyrimidine ring with an average value of 0.040 and 0.041° for compound I using the 6-31+G and 6-31++G basis sets, respectively. The average values of *d* are 12.28, 12.23, and 12.29° using the basis sets 6-31+G**, 6-31++G**, and 6-311++G**, respectively. In other words, the addition of polarization functions to the basis set resulted in the expected pyramidal geometry for the NH_2 group. For compound II, the average values of *d* are 0.012 and 0.012° using the 6-31+G and 6-31++G basis sets, respectively, while they are 0.506, 0.439, and 0.372° using the 6-31+G**, 6-31++G**, and 6-311++G** basis sets, respectively. These results show that the B3LYP method predict nearly a totally planar geometry for compound II. Better treatment of electron correlation problem in the MP2 method resulted in more reasonable values of *d*.

Generally, on going from the 6-31+G to the 6-31+G** basis sets and also from 6-31++G to 6-31++G** basis sets, the calculated *r* values decreased using either the MP2 or the B3LYP methods. This indicates that addition of d-type polarization functions on non-hydrogen atoms and p-type polarization functions on hydrogen atoms leads to a decrease in the values of the calculated *r* values. Also, the calculated values of *a* increased with nearly no change in the ring planarity shown by the calculated *d* going from 6-31+G to 6-31+G** or from 6-31++G to 6-31++G**. The same findings are found when using the 6-311++G** basis set. It is well known that the optimized geometries calculated at the MP2 and B3LYP levels of theory have a higher accuracy than those predicted at the HF level. They are close to each other[45–47] and in good agreement with experimental geometries.

Basis Set and Ground State Properties: The MP2 and B3LYP calculated ground state properties, namely, the total electronic energy, energies of the HOMO and LUMO levels, and the dipole moment for compounds I and II with all the basis sets are reported in Table 3. As expected, the addition of polarization functions leads to a stabilization of about 0.5 au using the MP2 method and about 0.1 au using the B3LYP method. This may be related to better handling the electron correlation in the MP2 calculations. It is worth noting that the MP2 calculated HOMO and LUMO energies reported in Table 3 indicate that the addition of highly diffuse s function on each hydrogen atom has a larger effect than that resulting from the addition of polarization functions on hydrogen or non-hydrogen atoms. The HOMO–LUMO energy gap for compound I was calculated to be 10.912, 10.145, 10.192, and 10.923 eV using the basis sets 6-31+G, 6-31++G, 6-31++G**, and 6-31+G**, respectively. For compound II similar effects are found, and the energy gap was calculated to be 11.446, 10.865, 10.743, and 11.283 eV using the same basis sets, respectively.

On the other hand, the addition of either highly diffuse s function on each hydrogen or polarization functions on hydrogen or non-hydrogen atoms was found to have a slight effect on the HOMO–LUMO energy gap using the B3LYP method. For compound I, the calculated HOMO–LUMO energy gap was found to be 5.183, 5.182, 5.257, and 5.258 eV, while the calculated values for compound II were 5.347, 5.347, 5.341, and 5.340 eV, and all of the values were obtained using the 6-31+G, 6-31++G, 6-31++G**, and 6-31+G** basis sets respectively. In case of using the 6-311++G** basis set, the MP2 calculated HOMO–LUMO energy gap was found to be 10.197 and 10.75 eV for compounds I and II, respectively, and the corresponding B3LYP calculated values were 5.255 and 5.354 eV, respectively.

Table 4 lists the calculated atomic charges using both MP2 and B3LYP methods. The values listed in this table indicate a net electronic accumulation mainly on the nitrogen atoms and the carbons attached to them. The net charge on the NH_2 nitrogen is the largest, as expected, either for compound I or compound II for all basis sets used. It seems that, as the basis set becomes more extended, electron accumulation on the ring atoms increases at the expense of the amino nitrogen atom electrons. The MP2 calculated net atomic charge on the amino nitrogen atom is calculated to be −0.705, −0.581, −0.540, −0.446, and −0.286 electrons for compound I using the 6-31+G, 6-31++G, 6-31++G**, 6-31+G**, and 6-311++G**, respectively, while −0.740, −0.627, −0.535, −0.442, and −0.306 electrons for compound II, respectively. The smallest basis set used 6-31+G predicts the highest negative charge on the amino nitrogen atom. The same trend is obtained using the B3LYP method with the highest negative charges on the amino nitrogen atom being −0.655 and −0.664 electrons for compound I and II, respectively, using the 6-31+G basis set. These changes in calculated net atomic charges as the basis set is extended are compatible with different

Table 3. MP2 and B3LYP Calculated Ground State Properties of Compounds I and II Using Different Extended Basis Sets

		MP2			
		E/au	HOMO/eV	LUMO/eV	μ/D
6-31+G	I	−318.287160	−9.051	1.861	1.1994
	II	−1236.134800	−9.851	1.595	1.5923
6-31++G	I	−318.287896	−9.054	1.091	1.2163
	II	−1236.135396	−9.850	1.015	1.5967
6-31+G**	I	−318.783637	−9.092	1.831	1.3872
	II	−1236.839755	−9.670	1.613	1.2454
6-31++G**	I	−318.784160	−9.092	1.100	1.3888
	II	−1236.840213	−9.670	1.073	1.2420
6-311++G**	I	−318.884292	−9.119	1.078	1.4044
	II	−1237.009739	−9.684	1.066	1.2209
		B3LYP			
		E/au	HOMO/eV	LUMO/eV	μ/D
6-31+G	I	−319.610101	−6.513	−1.330	0.3597
	II	−1238.762609	−7.258	−1.911	2.1573
6-31++G	I	−319.610370	−6.511	−1.329	0.3567
	II	−1238.762840	−7.258	−1.911	2.1596
6-31+G**	I	−319.722319	−6.497	−1.239	0.5765
	II	−1238.915858	−7.019	−1.679	1.8010
6-31++G**	I	−319.722466	−6.497	−1.240	0.5734
	II	−1238.915965	−7.020	−1.679	1.8003
6-311++G**	I	−319.789464	−6.548	−1.293	0.5781
	II	−1239.040474	−7.068	−1.714	1.8151

Table 4. MP2 and B3LYP Mulliken Atomic Charges for Compounds I and II Using Different Extended Basis Sets

	MP2									
	6-31+G		6-31++G		6-31+G**		6-31++G**		6-311++G**	
Center	I	II	I	II	I	II	I	II	I	II
1	−0.237	−0.086	−0.245	−0.100	−0.274	−0.176	−0.287	−0.189	−0.150	+0.006
2	+0.093	+0.195	−0.134	+0.027	+0.224	+0.322	+0.084	+0.242	−0.223	+0.059
3	−0.237	−0.086	−0.245	−0.100	−0.274	−0.176	−0.287	−0.189	−0.150	+0.006
4	−0.128	−0.230	−0.037	−0.120	−0.058	−0.217	+0.031	−0.153	−0.030	−0.679
5	−0.068	−0.301	−0.255	−0.470	−0.111	−0.059	−0.224	−0.165	−0.268	+0.159
6	−0.128	−0.230	−0.037	−0.120	−0.058	−0.217	+0.031	−0.152	−0.030	−0.679
7	−0.705	−0.740	−0.581	−0.627	−0.540	−0.535	−0.446	−0.442	−0.286	−0.306
8	+0.205	+0.193	+0.238	+0.178	+0.151	+0.108	+0.150	+0.100	+0.210	+0.311
9	+0.219	+0.264	+0.230	+0.264	+0.170	+0.205	+0.147	+0.174	+0.173	+0.237
10	+0.205	+0.193	+0.238	+0.178	+0.151	+0.108	+0.150	+0.100	+0.210	+0.311
11	+0.391	+0.413	+0.414	+0.444	+0.310	+0.318	+0.325	+0.337	+0.271	+0.287
12	+0.391	+0.413	+0.414	+0.444	+0.310	+0.318	+0.325	+0.337	+0.271	+0.287
					B3LYP					
1	−0.266	−0.097	−0.275	−0.122	−0.310	−0.187	−0.327	−0.214	−0.192	−0.024
2	+0.088	+0.185	−0.197	−0.012	+0.286	+0.494	+0.051	+0.374	−0.154	+0.142
3	−0.266	−0.097	−0.275	−0.122	−0.310	−0.187	−0.327	−0.214	−0.192	−0.024
4	−0.118	−0.225	−0.016	−0.169	−0.068	−0.206	+0.065	−0.197	−0.022	−0.707
5	+0.002	−0.234	−0.222	−0.324	−0.009	−0.056	−0.211	−0.082	−0.221	+0.065
6	−0.118	−0.225	−0.016	−0.169	−0.068	−0.206	+0.065	−0.197	−0.022	−0.707
7	−0.655	−0.664	−0.516	−0.527	−0.530	−0.560	−0.403	−0.430	−0.266	−0.352
8	+0.188	+0.164	+0.234	+0.157	+0.130	+0.048	+0.146	+0.045	+0.186	+0.394
9	+0.189	+0.235	+0.214	+0.257	+0.133	+0.169	+0.125	+0.163	+0.151	+0.203
10	+0.188	+0.165	+0.234	+0.157	+0.130	+0.048	+0.146	+0.045	+0.186	+0.394
11	+0.384	+0.397	+0.418	+0.436	+0.308	+0.321	+0.334	+0.353	+0.273	+0.308
12	+0.384	+0.397	+0.418	+0.436	+0.308	+0.321	+0.334	+0.354	+0.273	+0.308

Table 5. MP2 and B3LYP Optimum Geometries for the Dimers III, IV, and V Using 6-311++G** Basis Set

		III		IV	V
		MP2	B3LYP	B3LYP	B3LYP
r[a)]	1-2	1.3533	1.3551	1.3548	1.3563
	1-6	1.3403	1.3334	1.3323	1.3173
	2-3	1.3507	1.3512	1.3520	1.3513
	2-7	1.3641	1.3477	1.3481	1.3411
	3-4	1.3357	1.3266	1.3269	1.3105
	4-5	1.3971	1.3952	1.3949	1.3959
	4-8	1.0885	1.0872	1.0874	1.7524
	7-11	1.0096	1.0057	1.0057	1.0063
	7-12	1.0187	1.0166	1.0222	1.0197
	13-14	1.3550	1.3558	1.3547	1.3563
	13-18	1.3258	1.3161	1.3323	1.3173
	14-15	1.3524	1.3527	1.3520	1.3513
	14-19	1.3524	1.3410	1.3481	1.3411
	15-16	1.3228	1.3103	1.3269	1.3105
	16-17	1.3967	1.3953	1.3949	1.3959
	16-20	1.7300	1.7542	1.0874	1.7524
	19-23	1.0089	1.0064	1.0057	1.0063
	19-24	1.0250	1.0272	1.0220	1.0197
	12-13	2.0497	2.0851	2.0180	2.0442
	1-24	1.9682	1.9687	2.0203	2.0435
	7-13	3.0640	3.1006	3.0402	3.0635
	1-19	2.9919	2.9960	3.0422	3.0629
a[a)]	2-1-6	116.281	116.409	116.405	115.974
	1-2-3	125.766	125.123	125.154	124.654
	1-2-7	117.048	117.646	117.618	117.782
	2-3-4	116.205	116.519	116.477	116.297
	3-4-5	122.981	121.439	123.200	124.784
	2-7-12	116.709	120.403	121.568	121.442
	11-7-12	116.890	116.012	120.853	120.324
	14-13-18	115.761	124.605	116.407	115.974
	13-14-15	125.574	124.840	125.154	124.655
	13-14-19	116.931	116.272	117.611	117.771
	14-15-16	115.714	117.871	116.476	116.295
	15-16-17	124.501	121.776	123.201	124.785
	14-19-24	118.044	120.772	121.563	121.419
	23-19-24	119.367	116.409	120.846	120.335
	7-12-13	173.502	176.638	179.450	178.038
	12-13-14	120.609	121.475	121.419	122.707
	1-24-19	176.424	179.999	179.373	178.111
	2-1-24	121.556	123.157	121.383	122.693
d[a)]	7-2-1-6	177.313	179.992	179.975	179.982
	7-2-3-4	176.952	179.978	179.973	179.986
	11-7-2-1	165.624	179.970	179.992	179.977
	11-7-2-3	16.870	0.049	0.015	0.021
	12-7-2-1	23.557	0.048	0.040	0.016
	12-7-2-3	158.936	179.971	179.967	179.981
	19-14-13-18	176.652	179.991	179.991	179.985
	19-14-15-16	176.507	179.997	179.987	179.988
	23-19-14-13	169.052	179.915	179.905	179.988
	23-19-14-15	13.190	0.115	0.111	0.011
	24-19-14-13	18.035	0.292	0.160	0.011
	24-19-14-13	164.207	179.738	179.856	179.988
	13-12-7-2	35.936	1.058	0.550	8.263
	14-13-12-7	13.818	1.081	0.367	7.823
	15-14-13-12	166.838	179.8	179.895	179.651
	1-24-19-14	18.790	4.430	12.732	7.658
	2-1-24-19	27.038	4.193	12.422	7.192
	24-1-2-3	170.629	179.996	179.875	179.608

a) r (Å), a (degree), d (degree).

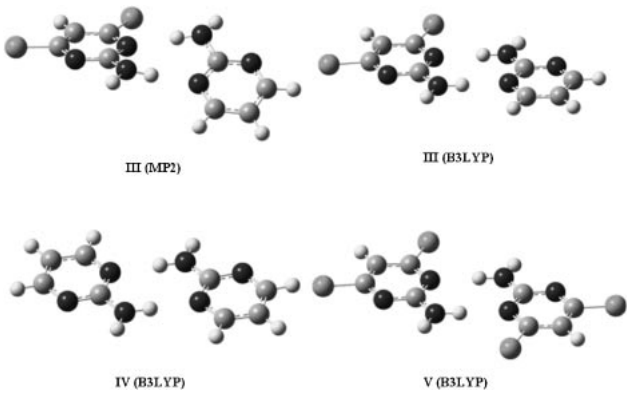

Fig. 2. MP2 and B3LYP geometrical approaches of the monomers in the dimers III, IV, and V using 6-311++G** basis set.

bonding multiplicity and degree of electronic delocalization. The calculated net atomic charges on N(1) and N(3) becomes more negative while that on N(7) becomes less negative as a highly diffuse s function and also p-type polarization functions on the hydrogen atoms together with d-type polarization functions on non-hydrogen atoms are added. The negative charges on these N atoms are the smallest when using the 6-311++G** basis set.

Dimers. A full geometry optimization has been performed to obtain the most favorable dimer interactions for compounds I and II. The dimer formed between I and II is denoted as III, while the dimer of I is denoted as IV and that of II is donated as V. Calculations were performed at the MP2/6-311++G** and B3LYP/6-311++G** levels. The triple zeta valence AOs basis sets are suitable for electron correlation calculations in compounds with a lone pair of electrons and hydrogen-bonded dimers and having significant electron density at large distances from the nuclei. Because the 6-311++G** basis set gave reliable geometrical parameters as discussed in above section, for dimer III, MP2/6-311++G** as well as B3LYP/6-311++G** calculations to determine the optimum geometry were performed. It was found that the MP2/6-311++G** calculations on dimer III were very time consuming, while the B3LYP/6-311++G** calculations took much less computational time. Also, it is clear from Table 5 that the calculated optimum molecular geometries using these two methods for dimer III are only slightly different. Since the differences in calculated molecular geometries were small, time consuming MP2/6-311++G** calculations were not performed on the other dimers. In other words, we performed full geometry optimization for dimers IV and V using only B3LYP/6-311++G** calculations. The results of the calculations for the three dimers are reported in Table 5, and the optimized geometrical approaches of the monomers in the three dimers are schematically shown in Fig. 2.

From a comparison of Table 5 with the optimum monomer geometries in Tables 1 and 2, general trends in the changes in monomer geometries upon dimer formation were determined. As expected, appreciable changes took place in the environment of the >C–NH_2 moiety in each interacting molecule, while the other geometrical parameters showed only slight changes. For example, the r values for C–C, C–H, C–Cl, and

even the N–H bonds not involved in H-bond formation are nearly unaffected upon dimer formation. Referring to the numbering schemes of the monomers (Fig. 1), the *r* value for the C(2)–N(7) bond decreased while the *r* values for the H-bonded N–H, C(2)–N(3), and C(2)–N(1) bonds increased upon dimer formation. The value of *r*(N(1)–C(6)) is slightly affected while that for the N(3)–C(4) bond decreased. These trends are the same whether using MP2 or B3LYP methods. Concerning the bond angles, we only consider the changes in the >C–NH_2 moiety. The MP2 and the B3LYP calculated *a* value for N(1)–C(2)–N(3) decreased upon dimer formation in both compound I and II. On the other hand, the *a* for angles N(1)–C(2)–N(7), C(2)–N(7)–H(12), and H(11)–N(7)–H(12) in both compounds I and II showed a smaller increase upon dimer formation. Since the geometrical arrangements of the monomers in the dimers are far from planar and the dimer is strongly deformed in order to permit the formation of two H-bonds, the changes in the calculated *d* values are not discussed in detail; however, the calculated values of *d* are reported in Table 5. The effect of H-bond formation as one of the factors that determine the conformational stability was previously investigated.[48–50] The two N···N distances, i.e., N(7)···N(13) and N(1)···N(19), in dimers IV and V (Table 5) are equal, as expected, since the donor and the acceptor molecules are the same. The distances are calculated to be 3.04 Å for dimer IV and 3.06 Å for the dimer V. These values are in a good agreement with N···N bond distances for the cyclic dimer of 4-amino-2,6-dichloropyrimidine (3.09 Å) and for 2-amino-6-chloro-4-methylpyrimidine[44] (3.21 Å) determined from X-ray data. In dimer III, one molecule contains two chlorine atoms in the 4- and 6-positions, and the other contains hydrogen atoms. This caused a difference of 0.1 Å and about 0.06 Å between the two N···N distances calculated using the B3LYP method and MP2 method, respectively, Table 5. It is worth noting that the N(1)···N(19) distance, which is farthest from the chlorine atoms was nearly the same for both methods (2.992 Å for MP2; 2.996 Å for B3LYP). However, the MP2 and B3LYP calculated N(7)···N(13) distances are 3.064 and 3.101 Å, respectively. Generally, these MP2 and B3LYP calculated N···N distances using the 6-311++G** basis set for dimer III are in good agreement with those from X-ray data for other cyclic pyrimidine dimers.[44] The difference between MP2 and B3LYP calculated equilibrium distances can be rationalized by the difference in the way electron correlation is dealt with by these two methods. Of course, the N–H···N interaction plays an important role in the stabilization of the optimized dimer structures.

The calculated net atomic charges for the three dimers are shown in Fig. 4. These calculated charge densities, when compared with those calculated for the monomers, Fig. 3, indicated a charge transfer of 0.014 electrons from MP2 calculations from compound II to compound I in dimer III, while from B3LYP calculations, the value was 0.043 electrons. This is consistent with the calculated net atomic charges on the amino nitrogen atom for compounds I and II (Table 4). The MP2/6-311++G** calculated value for compound II is −0.306 electrons while −0.286 electrons for compound I. On the other hand, the B3LYP/6-311++G** calculated values show larger difference in the calculated amino nitrogen charge (II, −0.352 electrons; I, −0.266 electrons). Also, the MP2 calculated net

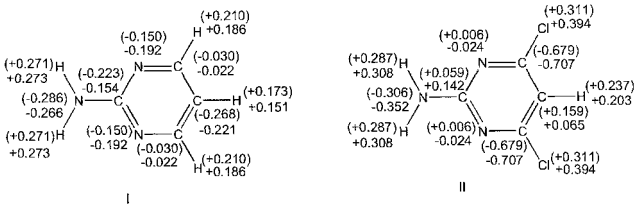

Fig. 3. MP2 and B3LYP net atomic charges for compounds I and II using 6-311++G** basis set (Values between brackets are for MP2).

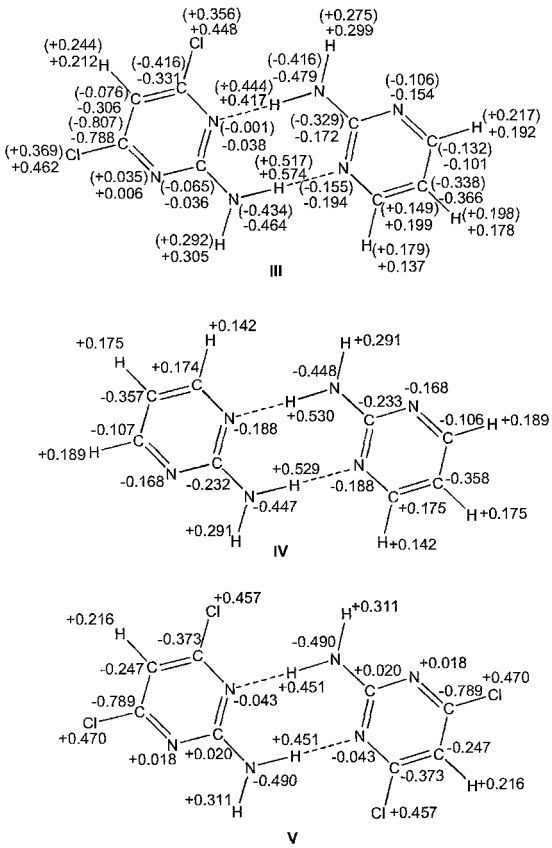

Fig. 4. MP2 and B3LYP net atomic charges for the dimers III, IV, and V using 6-311++G** basis set (Values between brackets are for MP2).

charge on the pyrimidine ring is −0.851 electrons for compound I and −1.128 electrons for compound II, and the B3LYP calculated net charge on the pyrimidine ring is −0.803 electrons for compound I and −1.255 electrons for compound II. This explains why the charge transfer upon dimer formation takes place from compound II to compound I and why the B3LYP calculated amount of charge transferred is larger than the MP2 calculated value. On the other hand and, no net charge transfer took place in case of dimers IV and V.

The MP2/6-311++G** calculated total energy of the dimer III is −1555.913988 au, with a dipole moment of 2.54 D, and the B3LYP/6-311++G** calculated value is −1558.846069 au with a dipole moment of 2.26 D. From the calculated monomer energies (Table 3), the MP2/6-311++G** method showed that the dimer III is stabilized by 12.523 kcal mol^{-1}. This stabilization energy is attributed

Table 6. BSSE Corrections at B3LYP Level for the Dimers III, IV, and V Using 6-311++G** Basis Set[a)]

	$E_A^{AB}(AB)$ /au	$E_B^{AB}(AB)$ /au	$E_A^{A}(AB)$ /au	$E_B^{B}(AB)$ /au	ΔE_{AB} /kcal mol^{-1}[b)]	δE^{BSSE} /kcal mol^{-1}	ΔE_{AB}^{BSSE} /kcal mol^{-1}
III	−319.789274	−1239.040241	−319.788817	−1239.039579	−10.1224	−0.7022	−9.4202
IV	−319.789073	−319.789081	−319.788658	−319.788665	−9.5771	−0.5215	−9.0556
V	−1239.040591	−1239.040593	−1239.039887	−1239.039890	−10.3301	−0.8829	−9.4472

a) Energies for monomers taken from Table 3. b) 1 au = 627.51 kcal mol^{-1}.

to the formation of two N–H···N H-bonds between I and II. Neglecting the slight difference in the calculated N···N distances, the energy of only one N–H···N H-bond amounts to 6.262 kcal mol^{-1}. The B3LYP/6-311++G** calculated dimer stabilization energy was found to be 10.122 kcal mol^{-1}, which means that only one N–H···N H-bond stabilizes the dimer by 5.061 kcal mol^{-1}. We have made basis set superposition error (BSSE) correction using the counterpoise method[39,40] by the following equation.

$$\Delta E_{AB}^{BSSE} = E_{AB}^{AB}(AB) - E_A^A(A) - E_B^B(B) - [E_A^{AB}(AB) + E_B^{AB}(AB) - E_A^A(AB) - E_B^B(AB)], \quad (1)$$

$$\Delta E_{AB}^{BSSE} = \Delta E_{AB} - \delta E^{BSSE}, \quad (2)$$

where the subscript refers to the system studied, the superscript refers to the basis set used to describe the system and the optimized geometry used is represented between the parentheses. The BSSE correction using B3LYP/6-311++G** was determined to be 0.702 kcal mol^{-1} (Table 6).

For dimer IV, the B3LYP/6-311++G** calculated total energy was found to be −639.594190 au, which amounts to a stabilization of 9.577 kcal mol^{-1} due to the formation of two N–H···N H-bonds between two molecules of I. Therefore, the stabilization energy due to the formation of only one N–H···N H-bond is 4.788 kcal mol^{-1}. The BSSE for this dimer was determined to be 0.521 kcal mol^{-1}. For the dimer V, the B3LYP/6-311++G** calculated total energy was found to be −2478.0974 au. This value, when compared with double the B3LYP/6-311++G** energy of compound II, afforded a stabilization energy of 10.330 kcal mol^{-1} corresponding also to two N–H···N H-bonds, or 5.165 kcal mol^{-1} per one H-bond. The calculated BSSE value was found to be 0.883 kcal mol^{-1}.

The influence of chlorine substitutents on the pyrimidine ring on the proton donor ability towards H-bond formation and parameters of the amino group of 2-aminopyrimidine as well as other electronic structural properties have been investigated.[51,52] It was shown that chlorine substitutents at the 4- and 6-positions of I significantly influence the donor ability of the amino group to form H-bonds. B3LYP/6-31+G** calculations of the charge redistribution upon H-bond formation have been performed and the charge-transfer process between the proton-donor and proton-acceptor molecules has been discussed.[51] The calculated values of the net atomic charges on going from compound I to compound II show that chlorine substitution in positions 4 and 6 causes an increase in the negative charge on the amino group. This observation is true using both MP2 and B3LYP methods and with all the extended basis sets used here. Our results show that, after the BSSE correction, the B3LYP/6-311++G** calculated stabilization energy per H-bond are 4.528, 4.668, and 4.723 kcal mol^{-1} for the dimers IV, III, and V, respectively. This leads to an important conclusion: substituting chlorine atom onto the pyrimidine ring of I increases the ability of the NH_2 group to form intermolecular H-bonds. Because the B3LYP/6-311++G** calculated dipole moment (Table 3) of compound I is smaller than that calculated for compound II, the dipole–dipole interaction between monomers upon dimer formation will increase upon chlorine substitution in the pyrimidine ring. This confirms the above conclusion.

Conclusion

The results reported here in this study suggest that both MP2(FC) and B3LYP methods using the 6-311++G** basis set are capable of accurately predicting the energies and molecular geometries of the possible intermolecular dimers of I and its 4,6-dichloro derivative.

The calculations show that the pyrimidine ring assumes a somewhat deformed but strictly planar hexagon, confirming the aromaticity of the pyrimidine ring. The addition of polarization functions to the basis set showed that geometry of the NH_2 group is pyramidal. The values of *r* were found to decrease as a result of the addition of d-type polarization functions on non-hydrogen atoms and p-type polarization functions on hydrogen atoms. This also leads to a more negative total electronic energy using the MP2 method (0.5 au) as compared to that using the B3LYP method (0.1 au). The effect on the HOMO–LUMO energy gap is also large using MP2 method than in case of B3LYP method. It seems that as the basis set is extended, electron accumulation on the ring atoms increases at the expense of the amino nitrogen atom.

The optimum dimer geometry by MP2 as well as the B3LYP is that in which two N–H···N intermolecular H-bonds have formed with appreciable changes in monomer bond lengths and angles, especially in the area near the >C–NH_2 moiety in each interacting molecule. The H-bond N···N distance is around 3.0 Å in a good agreement with that determined from X-ray analysis. The substitution of chlorine atoms onto the pyrimidine ring was found to increase the ability of the NH_2 group to form H-bonds.

Our results show that, after BSSE correction, the B3LYP/6-311++G** calculated stabilization energy per H-bond is approximately 4.5 kcal mol^{-1} for the studied dimers.

References

The calculations were done on an IBM Pentium4 PC with 2.8 GHz CPU, 1 MB Cash Memory and 1 GB RAM.

1 B. Pullman, A. Pullman, *Adv. Heterocycl. Chem.* **1971**, *13*, 77.

2 M. D. Topal, J. R. Fresco, *Nature* **1976**, *263*, 285; **1976**, *263*, 289.

3 a) G. Lauer, W. Schäfer, A. Schweig, *Tetrahedron Lett.* **1975**, *16*, 3939. b) D. Dougherty, K. Wittel, J. Meeks, S. P. McGlynn, *J. Am. Chem. Soc.* **1976**, *98*, 3815.
4 M. Fujii, T. Tamura, N. Mikami, M. Ito, *Chem. Phys. Lett.* **1986**, *126*, 583.
5 R. C. Lord, G. J. Thomas, *Spectrochim. Acta, Part A* **1967**, *23*, 2551.
6 R. D. Brown, P. D. Godfrey, D. McNaughton, A. P. Pierlot, *J. Am. Chem. Soc.* **1988**, *110*, 2329.
7 A. A. Hasanein, G. M. El-Subruiti, G. O. Younes, M. H. Sroor, *J. Solution Chem.* **2004**, *33*, 1481.
8 Y. Tsuchiya, M. Fujii, M. Ito, *J. Phys. Chem.* **1988**, *92*, 1760.
9 M. Kubota, T. Kobayashi, *J. Electron Spectrosc. Relat. Phenom.* **1996**, *82*, 61.
10 S. Chin, I. Scot, K. Szczepaniak, W. B. Person, *J. Am. Chem. Soc.* **1984**, *106*, 3415.
11 a) T. J. Zielinski, D. L. Breen, R. Rein, *J. Am. Chem. Soc.* **1978**, *100*, 6266. b) M. J. Scanlan, I. H. Hillier, *J. Am. Chem. Soc.* **1984**, *106*, 3737. c) U. J. Norinder, *THEOCHEM* **1987**, *151*, 259.
12 a) J. S. Kwiatkowski, R. J. Bartlett, W. B. Person, *J. Am. Chem. Soc.* **1988**, *110*, 2353. b) I. R. Gould, N. A. Burton, R. J. Hall, I. H. Hillier, *THEOCHEM* **1995**, *331*, 147.
13 a) J. Leszczynski, *J. Phys. Chem.* **1992**, *96*, 1649. b) A. Leś, L. Adamowicz, *J. Phys. Chem.* **1990**, *94*, 7021.
14 a) M. Monshi, K. Al-Farhan, S. Al-Resayes, A. Ghaith, A. A. Hasanein, *Spectrochim. Acta, Part A* **1997**, *53*, 2669. b) L. Paglieri, G. Corongin, D. A. Estrin, *Int. J. Quantum Chem.* **1995**, *56*, 615.
15 O. V. Shishkin, *J. Mol. Struct.* **1998**, *447*, 1.
16 D. Leitner, W. Schröder, K. Weisz, *J. Am. Chem. Soc.* **1998**, *120*, 7123.
17 G. E. Plum, K. J. Breslauer, *J. Mol. Biol.* **1995**, *248*, 679.
18 M. Orozco, B. Hernández, F. J. Luque, *J. Phys. Chem. B* **1998**, *102*, 5228.
19 C. Colominas, F. J. Luque, M. Orozco, *J. Am. Chem. Soc.* **1996**, *118*, 6811.
20 P. Hobza, J. Šponer, *Chem. Rev.* **1999**, *99*, 3247.
21 Y. Podolyan, Y. V. Rubin, J. Leszczynski, *J. Phys. Chem. A* **2000**, *104*, 9964.
22 L. Gorb, Y. Podolyan, J. Leszczynski, *THEOCHEM* **1999**, *487*, 47.
23 N. U. Zhanpeisov, J. Šponer, J. Leszczynski, *J. Phys. Chem. A* **1998**, *102*, 10374.
24 M. Orozco, F. J. Luque, *J. Am. Chem. Soc.* **1995**, *117*, 1378.
25 B. Hernández, F. J. Luque, M. Orozco, *J. Org. Chem.* **1996**, *61*, 5964.
26 C. Alhambra, F. J. Luque, J. Estelrich, M. Orozco, *J. Org. Chem.* **1995**, *60*, 969.
27 G. Fogarasi, *J. Mol. Struct.* **1997**, *413–414*, 271.
28 J. Leszczynski, *J. Phys. Chem.* **1992**, *96*, 1649.
29 J. Leszczynski, *J. Phys. Chem. A* **1998**, *102*, 2357.
30 R. Kobayashi, *J. Phys. Chem. A* **1998**, *102*, 10813.
31 J. Leszczynski, in *The Encyclopedia of Computational Chemistry*, ed. by P. V. R. Schelyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer, P. R. Schreiner, John Wiley & Sons, Chichester, **1998**.
32 F. J. Luque, J. M. López-Bes, J. Cemelí, M. Aróztegui, M. Orozco, *Theor. Chem. Acc.* **1997**, *96*, 105.
33 G. C. Shields, C. A. Laughton, M. Orozco, *J. Am. Chem. Soc.* **1997**, *119*, 7463.
34 a) P. Hobza, R. Zahradnik, *Chem. Rev.* **1988**, *88*, 871. b) J. Šponer, J. Leszczyński, P. Hobza, *J. Phys. Chem.* **1996**, *100*, 5590. c) P. Hobza, J. Šponer, M. Polášek, *J. Am. Chem. Soc.* **1995**, *117*, 792.
35 M. Rueda, F. J. Luque, J. M. López, M. Orozco, *J. Phys. Chem. A* **2001**, *105*, 6575.
36 S. Al-Resayes, K. Al-Farhan, M. Monshi, A. A. Hasanein, *J. Indian Chem. Soc.* **1998**, *75*, 506.
37 C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
38 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, Jr., K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defress, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94 (Rev. E.3)*, Gaussian Inc., Pittsburgh, PA, **1995**.
39 S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553.
40 J. G. C. M. van Duijneveldt-van de Rijdt, F. B. van Duijneveldt, *J. Mol. Struct.* **1982**, *89*, 185.
41 *Tables of Interatomic Distances and Configuration of Ions, and Supplement, Special Publication No. 18*, The Chemical Society, London, **1965**.
42 C. J. B. Clews, W. Cochran, *Acta Crystallogr.* **1948**, *1*, 4.
43 C. J. B. Clews, W. Cochran, *Acta Crystallogr.* **1949**, *2*, 46.
44 D. Voet, A. Rich, *The Crystal Structure of Purines, Pyrimidines and Their Intermolecular Complexes* in *Progress in Nucleic Acid Research and Molecular Biology*, ed. by J. N. Davidson, W. E. Cohn, Acad. Press, New York, **1970**, Vol. 10, pp. 183–265.
45 A. A. El-Azhary, H. U. Suter, *J. Phys. Chem.* **1996**, *100*, 15056.
46 B. G. Johnson, P. M. W. Gill, J. A. Pople, *J. Chem. Phys.* **1993**, *98*, 5612.
47 J. Catalán, J. L. G. dePaz, *J. Mol. Struct.* **1997**, *401*, 189.
48 P. Bultinck, A. Goeminne, Van de Vondel, *THEOCHEM* **1999**, *467*, 211.
49 P. Bultinck, C. Van Alsenoy, A. Goeminne, Van de Vondel, *J. Phys. Chem. A* **2000**, *104*, 11801.
50 P. Bultinck, C. Van Alsenoy, A. Goeminne, Van de Vondel, *J. Phys. Chem. A* **2001**, *105*, 9203.
51 V. E. Borisenko, S. A. Krekov, M. A. Niyazova, A. Koll, P. Lipkowski, *Vib. Spectrosc.* **2005**, *37*, 97.
52 D. V. Subbaiah, M. S. Sastry, V. Ramamurthy, *THEOCHEM* **1982**, *87*, 105.