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Molecular Complexes of Pentazolo[1,2-*a*]pentazole, N_8

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A theoretical study of the complexes formed by pentazolo[1,2-*a*]pentazole, N_8, with neutral electron donors, hydrogen-bond donors, and anions has been carried out at the B3LYP and MP2 computational levels. In addition, the clusters formed by two, three, and four molecules of N_8 have been studied. The results show that, in general, the interaction of the central N−N bond is preferred over the formation of a HB complex with neutral molecules. A comparison of the energetic results for the N_8 complexes obtained in the present article with those for analogous complexes of C_6F_6 demonstrates that the N_8 complexes exhibit a stronger interaction with both neutral and anionic systems. Small cooperative effects are observed in the calculated clusters of N_8.

Introduction

In the search for new allotropes of nitrogen, N_8 has attracted a great deal of attention.[1−8] Two structures have been postulated to be the most stable: the azidopentazole (**1**) and the octaazapentalene (pentazolo[1,2-*a*]pentazole) (**2**). The most recent theoretical studies indicate the former to be more stable than the latter.[2,6−8] However, our interest in azapentalenes[9,10] and in pentazoles[11,12] has driven us to study the possible complexes formed by **2** and, in particular, those corresponding to electron donor/anions π-interactions.[13−23] Note also the great interest aroused by these high-energy green substances (on decomposition, they will release only dinitrogen).[24−28]

In the present article, the possible interactions of octaazapentalene with electron donors, HB donors, and anions have been considered. In addition, the dimers, trimers, and tetramers of the N_8 molecule have also been studied.

Methods

The geometry of the monomers and complexes has been fully optimized with the B3LYP[29,30] and MP2[31] computational methods and the 6-311++G(d,p) basis set[32] within the Gaussian-03 package.[33] Frequency calculations have been carried out at both computational methods to confirm that the structures obtained correspond to energetic minima.

The inherent basis set superposition error (BSSE) has been corrected using the full counterpoise method[34] as implemented in the Gaussian-03 program.

The analysis of the electron density has been carried out under the Atoms In Molecules (AIM) methodology[35,36] with the AIMPAC,[37] MORPHY98,[38] and AIM2000 programs.[39] Numerical integration within the atomic basins has been carried out to obtain the atomic contribution to the total charge, volume, and energy of the systems. On the basis of our experience,[40] default parameters have been used except in those cases where the integrated Laplacian is larger than 1×10^{-3} in absolute value. In those cases, small errors in the charge and energy of the system compared to ab initio results are obtained.

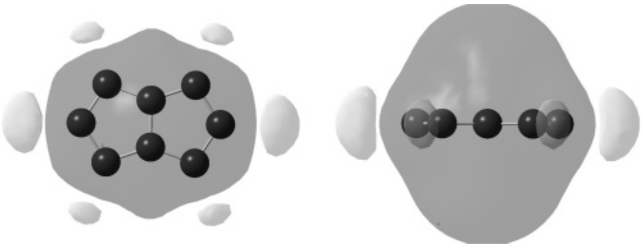

Figure 1. Two views of the molecular electrostatic potential at the ±0.02 au isosurface. Positive regions in dark and negative ones in light.

TABLE 1: Atomic Charges (*e*) and Values of the MEP Minima (au) Calculated at the B3LYP/6-311++G(d,p) Computational Level

atom	Mulliken	ChelpG	NBO	AIM	MEP minima
N1	−0.112	−0.417	−0.060	−0.007	−0.026
N2	−0.087	0.068	−0.027	0.001	−0.038
N3a	0.311	0.765	0.148	0.013	

The orbital interactions have been analyzed within the Natural Bond Orbital (NBO) framework[41] and the NBO 3.1 program.[42] This method allows the analyses of the interaction between filled and empty orbitals and associates them to charge-transfer processes.

Results and Discussion

N_8 Monomer. The molecular electrostatic potential (MEP) of the N_8 molecule (Figure 1) presents negative regions in the molecular plane close to the external nitrogen atoms, while a very positive region is obtained over the central nitrogen atoms (N3a, N6a). This situation resembles that obtained in the case of C_6F_6, wherein the region above the aromatic ring is positive, while negative regions preside in the molecular plane close the to fluorine atoms. In consequence, similar interactions can be expected for the C_6F_6 and N_8 molecules. The calculated values of the NICS(0) and NICS(1),[43] −13.75 and −12.79, respectively, indicate that the two rings of this molecule are more aromatic than benzene and pirrole.[44]

Four different methods have been used to evaluate the atomic charges (Table 1). However, none of them is able to properly account for the deeper minima in the MEP of N2 vs that of N1.

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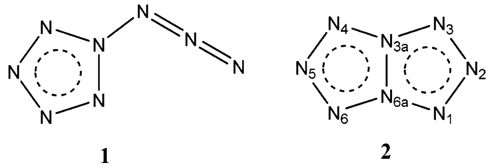
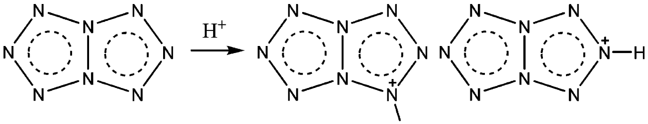
SCHEME 1: Schematic Representation of the Azidopentazole (1) and Octaazapentalene (2) Molecules[a]



[a] The numbering used for **2** in this article is indicated.

SCHEME 2



N1H$^+$ **N2H**$^+$

TABLE 2: Proton Affinity (kcal/mol)

protonation atom	B3LYP/ 6-311++G(d,p)	MP2/ 6-311++G(d,p)
N1	160.7	156.6
N2	166.2	167.2

TABLE 3: Corrected Interaction Energy (kcal/mol) and Results Obtained Previously for the Analogous Complexes with C_6F_6

complexes	symmetry	B3LYP/ 6-311++G(d,p) E_{I+BSSE}	MP2/ 6-311++G(d,p) E_{I+BSSE}	C_6F_6 complexes $E_{I+BSSE}{}^a$
N_8:CNH	C_{2v}	−3.85	−6.33	−1.52
N_8:NCH	C_{2v}	−3.79	−6.29	−1.65
N_8:FH	C_s	−2.64	−3.53	−1.23
N_8:OH_2	C_{2v}	−4.51	−6.18	

[a] Taken from ref 13 at the B3LYP/6-311++G(d,p) computational level.

Protonation on the N1 and N2 nitrogen atoms (Scheme 2) shows that the **N2H**$^+$ cation is more stable than the **N1H**$^+$ one by about 10 kcal/mol at the MP2/6-311++G(d,p) computational level (Table 2). These results are in agreement with the value of the MEP minima found in the proximity of both nitrogen atoms. The values obtained for the proton affinity (PA) indicate that this compound is about as basic as the water molecule in gas phase (the experimental PA of water is 165.2 kcal/mol).[45]

Complexes with Electron Donors. A series of small molecules that present free lone pairs and so could potentially interact with the central nitrogen atoms of N_8 has been examined. An energetic minimum is obtained for such complexes wherein the lone pair of the incoming molecule interacts with the positive region above the N3a−N6a bond, perpendicular to the molecular plane (Figure 2).

The energetic results (Table 3) show important differences between the two methods considered in this work. These differences could be due to the well-known poor description of dispersion forces by the DFT methods that should be very important in these kinds of complexes. The results show values larger than 6 kcal/mol for three of the cases and about half of this value for the complex with FH. Interestingly, comparison with analogous complexes of C_6F_6 shows that those with N_8 are significantly stronger than those with C_6F_6.

The NBO analysis does not show any important orbital interaction between the N_8 molecule and the electron donor systems. Thus, it can be concluded that the nature of the interaction is predominantly electrostatic.

The analysis of the electron density shows the presence of two bond critical points (bcp) between the electron donor molecule and the two central nitrogen atoms, N3a and N6a. Consequently and owing to topological reasons, a ring critical point (rcp) is also obtained. The characteristics of those points are gathered in Table 4. The proximity of the new rcp and bcp (as shown in Figure 3 for the N_8:NCH complex) and the similar value of the electron density and Laplacian indicate a low stability of the topological description. Thus, the calculated complex of N_8:NCH with a distance of 3.3 Å between the nitrogen atom of NCH and the center of the N3a−N6a bond exhibits a T-shape topology, without rcp, similar to those described for HB complexes with π- and σ-bonds.[46−48]

The values of the electron density at the bcp, as well as those of the Laplacian, indicate that these interactions correspond to closed-shell complexes. The integrated properties show a small electron transfer from the electron donor to the N_8 system, the results of the complex N_8:FH being reversed to the ones expected. An energy destabilization is observed for the electron donor molecules upon complexation, except for the FH complex, in agreement with previous reports that indicate a relationship between the charge and energy variations.[49,50] Finally, a small reduction of the volume is found due to the complex formation.

Complexes with HB Proton Donors. The N_8 molecule can also act via the N1 and N2 atoms (and the corresponding symmetric atoms) as a HB acceptor. The interaction energy values obtained for these complexes are gathered in Table 5. Attempts to obtain the corresponding complexes with water result in the electron donor complex already discussed in the previous sub-section of this paper.

In all cases, the HB complex with N2 is more stable than that with N1, in agreement with the results of the MEP minima calculations. In addition, the ratio N2/N1 for each case ranges between 1.40 and 1.48 at the MP2/6-311++G(d,p) computational level, while the MEP minima ratio is 1.45. This result agrees with the previous reports that indicate the possibility of using the MEP to derive the hydrogen-bond basicity.[51]

Comparison of the energies with those reported in the previous sub-section indicates that, with the exception of the

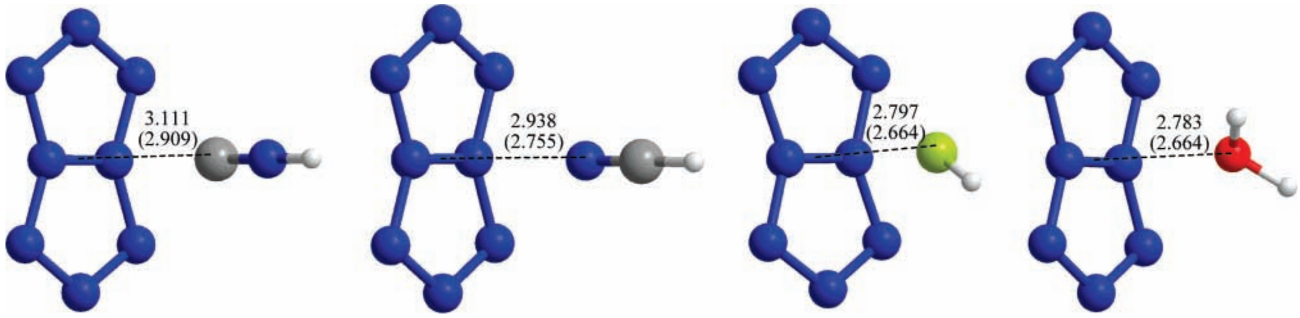


Figure 2. Geometry of the complexes between N_8 and electron donors (NCH, OH_2). The distances obtained between the interacting atom and the center of the N3a−N6a bond calculated at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels, in parentheses, are shown.

TABLE 4: Electron Density, Laplacian at the Intermolecular Critical Points (au), and Variation of the Integrated Properties of the Electron Donor System Calculated at the B3LYP/6-311++G(d,p) Computational Level

	bcp		rcp		electron donor molecule		
	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$	Δ charge (e)	ΔE (kcal/ mol)	Δ volume (au)
N_8:CNH	0.00800	0.0267	0.00799	0.0270	0.022	39.53	−9.52
N_8:NCH	0.00899	0.0347	0.00897	0.0351	0.012	39.68	−9.23
N_8:FH	0.00844	0.0384	0.00840	0.0390	−0.002	−23.86	−2.13
N_8:OH_2	0.01092	0.0454	0.01088	0.0463	0.006	0.75	−8.77

TABLE 5: Corrected Interaction Energy (kcal/mol), Second-Order Perturbation Energy, *E*(2), of the Nitrogen Lone Pair → *σ (HX) Interaction (kcal/mol), and Interatomic Distances of the HB Formed (Å)**

		B3LYP/ 6-311++G(d,p)		MP2/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)	MP2/ 6-311++G(d,p)
complex and HB site	symm.	$E_{\mathrm{I+BSSE}}$	$E(2)$	$E_{\mathrm{I+BSSE}}$	H···N distance	H···N distance
N_8:HCN(N1)	C_s	−1.38	3.29	−1.77	2.386	2.355
N_8:HCN(N2)	C_{2v}	−2.10	4.24	−2.62	2.323	2.299
N_8:HNC(N1)	C_s	−3.01	6.91	−3.12	2.099	2.072
N_8:HNC(N2)	C_{2v}	−3.96	8.72	−4.39	2.053	2.013
N_8:HF(N1)	C_s	−3.76	8.71	−3.10	1.913	1.964
N_8:HF(N2)	C_{2v}	−4.81	11.08	−4.42	1.877	1.895

FH molecule, the electron donor complex is preferred over HB formation with the peripheral nitrogen atoms.

The NBO analysis shows an orbital interaction between the lone pair of the nitrogen and the *σ** of the HB donor (Table 5). The energetic values of this orbital interaction are highly correlated with the interaction energy ($R^2 = 0.99$).

Furthermore, the N2 HB complexes present shorter interaction distances than their N1 counterparts in every case observed. This result is in agreement with the greater stability of the former complex for every HB donor studied here.

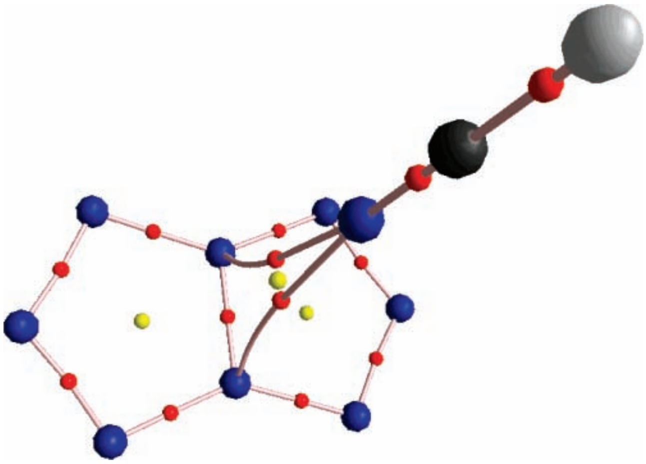


Figure 3. Molecular graph of the N_8:NCH complex. The bcp's are represented with red dots and the rcp's with yellow dots.

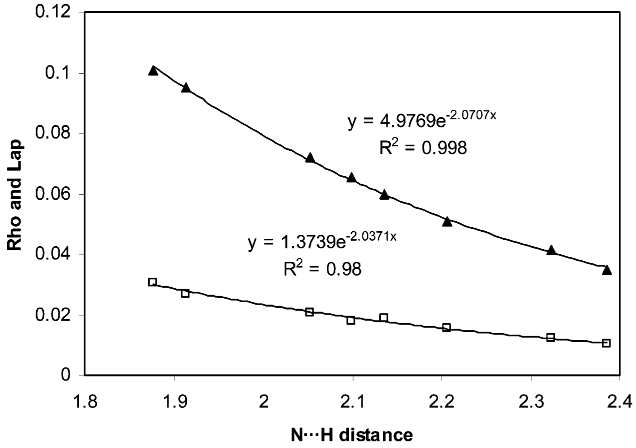


Figure 4. ρ (squares) and $\nabla^2 r$ (triangles) (au) of the HB critical points vs the interatomic distance (Å).

In all cases, the AIM analysis of the electron density of the HB complexes shows a new bcp. The values of the ρ and $\nabla^2 r$ are exponentially correlated with the HB distance (Figure 4), in agreement with previous reports for other HB complexes.[52−57]

Interaction with Anions. The complexes formed between the anions considered here and the N_8 molecule present C_{2v} symmetry, with the anions located above the center of the N3a−N6a bond. The distances obtained at the MP2 level (Table 6) range from 2.34 Å for the N_8:F^- complex to 2.84 Å for the N_8:Cl^- complex, while those computed at B3LYP level are slightly longer. The interaction with the ions results in the loss of planarity of the N_8 system, with the angle formed between the two rings in the strongest complex (N_8:F^-) being 173.4°, with the N2 atoms moving farther away from the anions. In

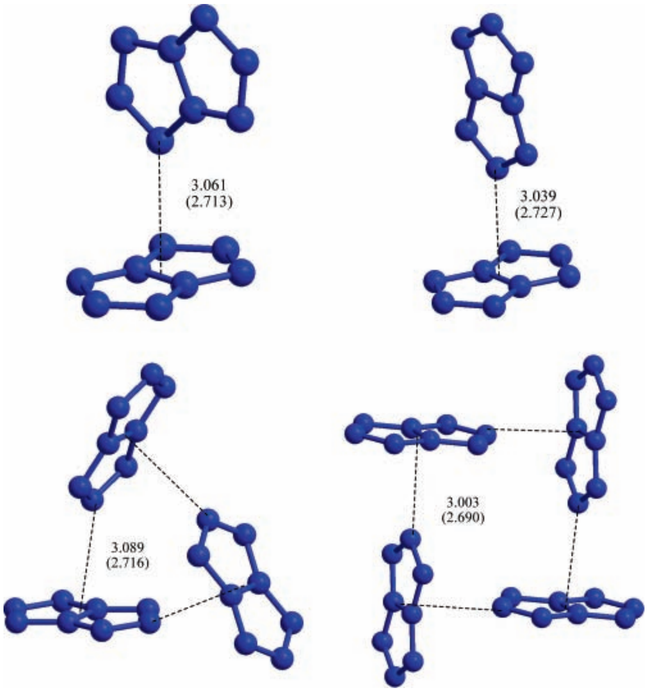


Figure 5. Dimers, trimer, and tetramer structures of N_8 clusters.The distances obtained between the interacting atom and the center of the N3a−N6a bond calculated at the B3LYP/6-311++G(d,p) and MP2/ 6-311++G(d,p) levels, in parentheses, are shown.

TABLE 6: Corrected Interaction Energy (kcal/mol) and Distance between the Interacting Atom and the Center of the N3a−N6a Bond (Å) for the Complexes between N_8 and Anions (Energetic values of the analogous C_6F_6 complexes have been included.)

complexes[a]	B3LYP/ 6-311++G(d,p) E_{I+BSSE}	MP2/ 6-311++G(d,p) E_{I+BSSE}	C_6F_6 complexes[b] E_{I+BSSE}	B3LYP/ 6-311++G(d,p) X···* Distance	MP2/ 6-311++G(d,p) X···* Distance
N_8:F$^-$	−26.83	−27.82	−17.31[c]	2.371	2.342
N_8:Cl$^-$	−15.12	−18.15	−12.52[c]	3.058	2.844
N_8:CN$^-$	−15.28	−19.10	−12.52[c]	2.907	2.767
N_8:NC$^-$	−16.31	−19.55	−13.14[d]	2.712	2.594
N_8:CCH$^-$	−17.72	−22.04	−15.07[d]	2.875	2.731
N_8:CNO$^-$	−14.45	−18.62	−12.43[d]	2.883	2.730
N_8:ONC$^-$	−14.83	−17.41	−11.42[d]	2.514	2.413

[a] The first atom after the N_8 is that pointing toward this molecule. [b] Results taken from ref 17. [c] MP2/6-311++G(d,p) results. [d] MP2/6-311+G(d,p) results.

TABLE 7: Electron Density, Laplacian at the Intermolecular Critical Points (au), and Variation of the Integrated Properties of the Anions Calculated at the B3LYP/6-311++G(d,p) Computational Level

	bcp		rcp		electron donor molecule		
system	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$	ΔE	Δ charge	Δ volume
N_8:F$^-$	0.0244	0.1078	0.0241	0.1141	−64.76	0.079	−35.2
N_8:Cl$^-$	0.0120	0.0399	0.0119	0.0409	−105.08	0.075	−43.8
N_8:CN$^-$	0.0131	0.0418	0.0130	0.0430	11.55	0.064	−28.7
N_8:NC$^-$	0.0151	0.0590	0.0150	0.0609	8.96	0.047	−26.3
N_8:CCH$^-$	0.0142	0.0457	0.0142	0.0473	27.77	0.080	−40.8
N_8:CNO$^-$	0.0129	0.0432	0.0128	0.0446	−5.09	0.059	−29.2
N_8:ONC$^-$	0.0161	0.0805	0.0157	0.0855	−9.86	0.037	−24.0

TABLE 8: Corrected Interaction Energy (kcal/mol) and Electron Density Properties (au) of the Intermolecular bcp Found in the N_8 Clusters

complexes	symmetry	B3LYP/ 6-311++G(d,p) E_{I+BSSE}	MP2/ 6-311++G(d,p) E_{I+BSSE}	ρ	$\nabla^2\rho$
$(N_8)_2$ (N1)	C_s	−1.11	−4.43	0.0074	0.0272
$(N_8)_2$ (N2)	C_{2v}	−1.62	−5.11	0.0079	0.0292
$(N_8)_3$	C_{3h}	−4.64	−15.66	0.0072	0.0260
$(N_8)_4$	C_{4h}	−7.70	−22.63	0.0086	0.0316

addition, a small increment of the aromaticity of the N_8 molecule is observed being the average value of the NICS(0) and NICS(1) in the complexes studied, 14.87 and 13.56, respectively.

The interaction energies span from −27.8 to −17.4 kcal/mol at the MP2/6-311++G(d,p) level. It is significant that they are always much larger than in analogous complexes of C_6F_6. In fact, a linear correlation (eq 1) can be obtained by comparing the interaction energies of both series:

$$E_{I+BSSE}(N_8{:}X) = 3.15 + 1.74[E_{I+BSSE}(C_6F_6{:}X)],\quad R^2 = 0.96,\ n = 7 \quad (1)$$

The slope of eq 1 indicates that the N_8:X$^-$ complexes are, in average, 1.7 times stronger than the corresponding C_6F_6:X$^-$ ones.

The analysis of the electron density shows features similar to those found in the case of the complexes between neutral electron donors and N_8; two degenerate bcp and a rcp (Table 7). As expected, the values of ρ and $\nabla^2 r$ are larger than those obtained for the complexes with neutral electron donors due to the shorter distance between the anions and the N_8 system. The integrated properties of the electron donor molecule show a charge transfer from the anion to the N_8 molecule of up to 0.08 e for the F(−) and CCH(−) complexes which is associated with an important reduction with the volume of these molecules. Regarding the variation of energy, for the halogen complexes a stabilization superior to the complexation energy is observed, while in the rest of these cases the variation is positive (energetic destabilization) or smaller than the complexation energy.

In order to analyze the importance of the electrostatic interaction in these complexes, the value of the MEP has been calculated for the isolated N_8 molecule in the position of the interacting anions. For the two monatomic anions, F$^-$ and Cl$^-$, the results obtained for the MEP (−27.92 and −16.05 kcal/mol at the B3LYP/6-311++G(d,p) level and −27.52 and −18.12 kcal/mol at the MP2/6-311++G(d,p) level, respectively) are almost identical to the corrected interaction energy listed in Table 6. Thus, for these systems, the electrostatic potential of the N_8 molecule is able to predict its interaction energy. For

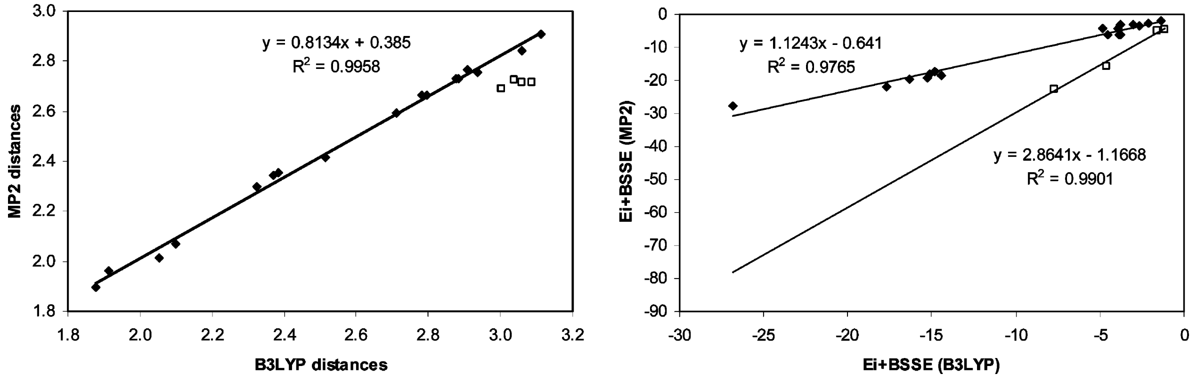


Figure 6. MP2 results (Å and kJ/mol) vs the corresponding B3LYP results. The open squares correspond to the N_8 clusters.

the polyatomic anions, the total negative charge is distributed along the whole system and this simplified model overestimates the predicted interaction energy.

N_8 Clusters. On the basis of the results obtained for the neutral systems, two configurations for the dimer have been considered (Figure 5), which corresponds to the interaction of the N1 and N2 with the N3a−N6a bond. Since the complex formed by the interaction of N2 with the N3a−N6a bond is the most stable (Table 8), this complex has been used as a basis to generate the trimer and tetramer. As mentioned before, the B3LYP method poorly described this interaction when compared to MP2, both geometrically and energetically. The MP2 results show a certain degree of cooperativity as the size of the N_8 cluster increases, especially in respect to the shortening of the N2···N3a−N6a distance.

The analysis of the electron density shows two distinct topologies for the two possible dimers; in the case of the interaction between the N1 and the nearest atom of the N3a−N6a bond one bcp is found, while in the case of the interaction between N2 and the N3a−N6a bond two bcp are found with a rcp close to the position of the former ones. The values of the electron density and Laplacian of the intermolecular bcp (Table 8) show typical properties of closed-shell interactions with small values of the electron density and positive and small values of the Laplacian.

General Aspects. The intermolecular distances obtained in all the complexes studied at the two computational levels have been compared and surprisingly a very good linear correlation has been found when the N_8 clusters are not included (Figure 6). In the same way, the energetic results present a good linear correlation when the N_8 clusters are considered as a different set. Thus, in a first approximation, the geometrical results at the MP2 level can be estimated using the corresponding B3LYP data.

In recent years, there has been increasing interest in the study of interactions between electronegative atoms.[58−64] In the systems considered, it can be found that six of them present intermolecular N···N interactions. In addition, the N_8 molecule presents three different N−N bonds. The electron density at the bcp of all these interactions, in the range between 1.3 and 3.1 Å, nicely fits a unique exponential relationship (eq 2):

$$\rho = 7.26 \times \exp(-2.20 \times \text{N−N distance}),\quad R^2 = 0.9997, n = 9 \quad (2)$$

Conclusion

The complexes where the pentazolo[1,2-*a*]pentazole, N_8, molecule interacts with neutral electron donors, HB donors, and anions have been studied theoretically using B3LYP and MP2 computational methods. The MEP of the isolated molecule shows the presence of a large positive region above the central N−N bond and negative regions close to the rest of the nitrogen atoms. Thus, the complexes formed by the neutral electron donors or anions interact with the central N−N bond, while hydrogen-bonded complexes present an interaction with the peripheral nitrogen atoms.

A comparison of the results obtained here between N_8 and anions and those previously reported for analogous complexes of C_6F_6 indicate that the former are, on average, 1.7 times stronger than the later. The formation of N_8 clusters, up to tetramers, has also been studied. The cyclic tetramer presents a small cooperative effect when compared to results obtained for the dimer.

In summary, N_8 is an aromatic, neutral, and apolar molecule that nevertheless presents two charged halves (−++−), making it a fascinating compound without equivalent in organic chemistry (the azide anion has related properties), thus deserving theoretical study.

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Supporting Information Available: Optimized structures of the complexes at the MP2/6-311++G(d,p) computational level. This material is available free of charge via the Internet at http://pubs.acs.org.

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