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THEORETICAL STUDY ON DIMERS OF 2,6-DIAMINO-3,5-DINITROPYRIDINE AND ITS *N*-OXIDE

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First-principle calculations are performed on the dimers of 2,6-diamino-3,5-dinitropyridine (ANPy) and its *N*-oxide (2,6-diamino-3,5-dinitropyridine-1-oxide, ANPyO). The dimers as well as the monomers are fully optimized by the DFT-B3LYP and HF methods in conjunction with 6-311G**, 6-311++G**, and cc-pVDZ basis sets. The N—O bond length of the pyridine *N*-oxide moiety decreases in the ANPyO dimer in the dimerization process, which results in a larger deformation energy of the ANPyO submolecule. This deformation prevents the submolecules from further close contact and the formation of strong H-bonds between the nitro and amino groups. The optimized intermolecular distances of the ANPyO dimer are in good agreement with the corresponding experimental values. There is a weak C—H···O hydrogen bond in the ANPyO dimer; the B3LYP method underestimates its binding energy. On the contrary, for the ANPy dimer, the binding energy obtained at the B3LYP level is larger than that obtained at the HF level. The individual O···H strength is stronger in the ANPy dimer than that in ANPyO, which is consistent with the O···H distance. The O···H—C type of the H-bond is stronger in the ANPyO dimer than the ordinary O···H—C bond due to the *N*-oxide oxygen atom bearing larger negative charges. The corrected binding energy for each hydrogen bond between nitro oxygen and amino hydrogen is about –5 kJ/mol in the ANPy dimer, which is stronger than that in the ANPyO dimer.

Keywords: 2,6-diamino-3,5-dinitropyridine, 2,6-diamino-3,5-dinitropyridine-1-oxide, intermolecular interaction, first-principle calculations, natural bond orbital.

INTRODUCTION

2,6-Diamino-3,5-dinitropyridine (ANPy, $C_5HN(NO_2)_2(NH_2)_2$) and its *N*-oxide (2,6-diamino-3,5-dinitropyridine-1-oxide, ANPyO, $C_5HNO(NO_2)_2(NH_2)_2$) are fresh insensitive high explosives (IHE) [1—3]. According to the literature, ANPyO has been prepared by mixed acid nitration of 2,6-diaminopyridine, followed by oxidation using hydrogen peroxide in acetic acid [4]. ANPy and ANPyO contain both the nitro groups as well as the amino groups (Fig. 1), making it an important explosive and raw material for preparing high energetic explosives [5, 6]. The structures of ANPy and ANPyO are similar to that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), making them potential insensitive high energy explosive candidates with heat resistance, low mechanical and thermal sensitivity [7]. The comprehensive performance of ANPyO is similar to that of a widely used TATB IHE, apart from a higher sensitivity for the former [4]. Furthermore, the cost of ANPyO is significantly lower than that of TATB. Compared to TATB, ANPyO has a higher performance-price ratio and is a promising candidate in the field of energetic materials. To date there have been few theoretical studies on ANPy and ANPyO. The electronic structures of polynitropyridines and their *N*-oxides for their gaseous states were calculated by Li et al. [2]. The behavior of molecular clusters is usually between

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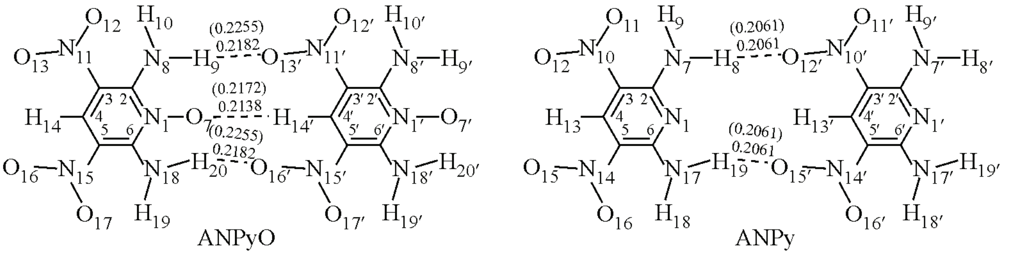

Fig. 1. Optimized structures of the dimers (data on dashed lines are the intermolecular distances at the B3LYP/6-311++G** level, and data in parenthesis are those at the HF/6-311++G** level)

two extremes: the gas phase and the crystal solid phase. Consequently, one can obtain valuable knowledge about the transition of these extremes by examining the properties of dimers or clusters. Proper characterization of these phenomena is thus crucial to the understanding of the behavior of dimers or clusters [8, 9]. The intermolecular forces control such diverse phenomena as diffusion, aggregation, and detonation. It is particularly necessary to study the intermolecular interaction. Although computations of gaseous molecules correctly predict some properties [10], it remains unknown from the viewpoint of the electronic structure in its dimer. The aim of this paper is to investigate theoretically the structures and the binding energies of the title dimers by first-principle methods. We also perform natural bond orbital (NBO) analyses [11, 12] to probe the origin of the interactions. This provides the fundamental information on the interactions of energetic systems.

COMPUTATIONAL METHODS

The DFT method deals with the electron correlation but is still computationally economic. With its B3LYP functional, both the structure and binding energy are depicted consistent with experiments for the systems of strong H-bonds [13, 14]. The initial structures of ANPy, ANPyO, and their corresponding homodimers were obtained from the Chem3D software [15]. The Chem3D software uses the standard geometrical data for molecular modeling and molecular mechanics and/or semi-empirical quantum methods for locating low energy conformations. Then, the structures obtained from Chem3D were fully optimized at the DFT-B3LYP and HF levels by the Berny method [16] with 6-311G**, 6-311++G**, and cc-pVDZ basis sets. In each structure, the existence of an energy minimum was confirmed by the absence of imaginary vibrational frequencies. The interaction energy of the complex is evaluated as the energy difference of the dimer and monomer. The basis sets commonly used to calculate the energies are far from being saturated. As a result, each subsystem in any complex will tend to lower its energy due to the use of the basis functions of another subsystem. The energies obtained at the equilibrium geometry of the complex for each subsystem are lower than those calculated at the same geometry with the basis functions of the respective subsystem alone. This energy difference is the so-called basis set superposition error (BSSE) that can be checked by the Boys and Bernardi counterpoise procedure (CP) [17, 18]. Natural bond orbital analyses and frequency calculations were performed on each optimized structure. The NBO interaction was analyzed, which revealed the origin of charge transfer and the intermolecular interaction. All quantum chemical calculations concerning the gaseous phase were performed with the Gaussian 03 suite of programs [19].

RESULTS AND DISCUSSION

Optimized geometries. Fig. 1 shows the optimized geometries of ANPyO and ANPy dimers at the B3LYP/6-311++G** and HF/6-311++G** levels. After the stationary points were located, vibrational frequencies were calculated in order to ascertain that each structure found corresponded to a minimum on the potential energy surfaces (no imaginary frequencies for both structures in Fig. 1). Both ANPyO and ANPy dimers possess approximately C_S symmetry. The ANPyO dimer (with hydrogen bond donors of two N—H and one C—H) has three intermolecular contacts with distances in a range of 0.21—0.23 nm. The ANPy dimer (with hydrogen bond donors of two N—H) has two inter-

Table 1

Bond lengths (nm) *of* ANPyO *and* ANPy *dimers* [a]

Bond	Length [b]	Length [c]	Bond	Length [b]	Length [c]
	ANPyO			ANPy	
N_8—H_9	0.1018 (0.1016)	0.1001 (0.1000)	N_7—H_8	0.1012 (0.1008)	0.0995 (0.0994)
N_1—O_7	0.1314 (0.1315)	0.1326 (0.1329)	N_{17}—H_{19}	0.1012 (0.1008)	0.0995 (0.0994)
N_{18}—H_{20}	0.1018 (0.1016)	0.1001 (0.1000)	$O_{12'}$—$N_{10'}$	0.1232 (0.1225)	0.1194 (0.1188)
$O_{13'}$—$N_{11'}$	0.1226 (0.1223)	0.1189 (0.1186)	$O_{15'}$—$N_{14'}$	0.1232 (0.1225)	0.1194 (0.1188)
$H_{14'}$—$C_{4'}$	0.1085 (0.1082)	0.1076 (0.1072)			
$O_{16'}$—$N_{15'}$	0.1226 (0.1223)	0.1189 (0.1186)			

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[a] Data in parenthesis are of monomer; atom numbering with a prime belongs to another submolecule.
[b] At the B3LYP/6-311++G** level.
[c] At the HF level.

molecular contacts with an identical distance of 0.206 nm. The optimized $N_8\cdots O_{13'}$ and $O_7\cdots C_{4'}$ distances are 0.3157 nm and 0.3104 nm respectively at the B3LYP/6-311++G** level. The respective values are 0.3209 nm and 0.3110 nm at the HF/6-311++G** level. These values are in good agreement with the corresponding experimental values of 0.323 nm and 0.315 nm [20]. The intermolecular O···H distances for ANPyO are only slightly longer at the HF/6-311++G** level than those at the B3LYP/6-311++G** level. As a whole, both HF and B3LYP methods produce rational intermolecular distances. As can be seen from Table 1, all the bonds adjacent to the intermolecular contacts elongate for ANPyO, except the N_1—O_7 bond. In contrast, the N_1—O_7 bond decreases in the dimerization process, which results in a larger deformation energy of the ANPyO submolecule. The deformation energies for the ANPyO submolecules are 1.1 kJ/mol (left submolecule of the ANPyO dimer in Fig. 1) and 0.7 kJ/mol (right) at the B3LYP/6-311+G** level. However, the deformation energies for the ANPy monomers are 0.6 kJ/mol (left submolecule) and 0.5 kJ/mol (right) at the same computational level. Similarly, all the bonds adjacent to the intermolecular contacts elongate for ANPy to facilitate the formation of hydrogen bonds. The ANPyO dimer has three longer H···O bonds with C—H and two N—H as hydrogen bond donors. The ANPy dimer has two shorter H···O bonds with two N—H as hydrogen bond donors. Judging by the intermolecular distances, number of contacts, and the type of a hydrogen bond donor, there is no large discrepancy in the binding energy of ANPyO and ANPy dimers.

Binding energies. Table 2 shows the binding energies of ANPyO and ANPy dimers at the DFT-B3LYP and HF levels, including the uncorrected and BSSE corrected binding energies ΔE and ΔE_C. The basis sets affect the binding energy; the B3LYP method is more dependent on the basis sets than the HF method. Of all the basis sets, the cc-pVDZ basis set produces a slightly larger binding energy. The corrected binding energy for ANPyO dimers is less than that for ANPy dimers at the B3LYP level. In contrast, the corrected binding energy for ANPyO dimers is larger than that for ANPy dimers at the HF level. Obviously, this contrary trend of the binding energy obtained from different methods is due to the fact that the DFT-type methods have only been successful so far for the intermolecular interactions dominated by a strong hydrogen bond [14, 21]. There is an extra weak C—H···O hydrogen bond in the ANPyO dimer in comparison with the ANPy dimer. However, the binding energy is smaller in the ANPyO dimer than that in the latter at the B3LYP level, indicating that the B3LYP method underestimates the binding energy for systems with weak hydrogen bonds of the C—H···O type, since it dose not include the spin kinetic energy density (τ_σ) in the exchange and correlation functional for the study of noncovalent interactions [22]. Consequently, for the ANPyO dimer, the binding energy obtained at the B3LYP level is smaller than that obtained at the HF level. On the con-

Table 2

Binding energies (*in* kJ/mol) *of the* ANPyO *and* ANPy *dimers at different computational levels* [a]

Methods	ANPyO		ANPy	
	ΔE	ΔE_C	ΔE	ΔE_C
B3LYP/6-311g**	–30.04	–23.61	–32.66	–27.91
B3LYP/6-311++g**	–24.05 (–45.76)	–21.37 (–36.53)	–27.83 (–41.83)	–25.48 (–34.64)
B3LYP/cc-pVDZ	–35.60	–25.21	–38.12	–30.44
HF/6-311g**	–28.09	–24.53	–25.83	–23.35
HF/6-311++g**	–28.09	–24.53	–25.31	–22.48
HF/cc-pVDZ	–32.50	–26.25	–28.20	–24.53

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[a] ΔE is the binding energy, ΔE_C is the binding energy with 50 % BSSE correction. Data in parenthesis are at the MP2/6-311++G**//B3LYP/6-311++G** level.

trary, for the ANPy dimer, the binding energy obtained at the B3LYP level is larger than that obtained at the HF level, since the B3LYP method adequately estimates the binding energy for a system dominated by a strong hydrogen bond (with N—H as a hydrogen bond donor in contrast to C—H). The corrected binding energies are –36.53 kJ/mol and –34.64 kJ/mol for the ANPyO and ANPy dimer, respectively at the MP2/6-311++G**//B3LYP/6-311++G** level. This indicates further that B3LYP produces rational intermolecular distances, but underestimates the binding energy for the ANPyO dimer. For the ANPy dimer, the absolute values of ΔE_C at the B3LYP level are much larger than those at the HF level, indicating the necessity of including electron correlation into the binding energy. Although there is no experimental binding energy to verify the accuracy of the predicted binding energy, we may say that the binding energy of –30.44 kJ/mol is reliable for the ANPy dimer (B3LYP/cc-pVDZ level), indirectly judging by the best experimental estimate of the dissociation energy (ca. 2×15 kJ/mol) of the water dimer [23]. The BSSE of the dimers at all the computational levels are in a range of 2.35 kJ/mol to 10.35 kJ/mol, indicating that it is essential to carry out the BSSE corrections.

Electron densities at hydrogen bond critical points. Based on the optimized structures at the B3LYP/6-311++G** and HF/6-311++G** levels, the electron densities at bond critical points and the ratio of $r_{O\cdots H}$ (or $r_{N\cdots H}$) to $r_{N—H}$ were calculated with the AIM 2000 program. The electron densities from the AIM theory are not sensitive to either the basis set or the induction of electron correlation [24]. As can be seen from Table 3, the ratios of the electron density on intermolecular O···H to that

Table 3

Electron densities (a.u.) *at hydrogen bond critical points at the* B3LYP/6-311++G** *level* [a]

H-bond	ρ [b]	ρ [c]	H-bond	ρ [b]	ρ [c]
ANPyO			ANPy		
$H_9\cdots O_{13'}$	0.0116 (0.0350)	0.0091 (0.0263)	$H_8\cdots O_{12'}$	0.0161 (0.0480)	0.0150 (0.0442)
$O_7\cdots H_{14'}$	0.0137 (0.0420)	0.0120 (0.0346)	$N_1\cdots H_{13'}$	0.0022 (0.0070)	0.0019 (0.0056)
$H_{20}\cdots O_{16'}$	0.0117 (0.0360)	0.0091 (0.0263)	$H_{19}\cdots O_{15'}$	0.0161 (0.0480)	0.0150 (0.0442)
$N_8—H_9$	0.3287 (1.000)	0.3466 (1.000)	$N_7—H_8$	0.3357 (1.000)	0.3394 (1.000)

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[a] Atom numbering with a prime belongs to another submolecule. Data in parenthesis are the ratio of O···H to $N_8—H_9$ for ANPyO, and O···H or N···H to $N_7—H_8$ for ANPy.

[b] At the B3LYP/6-311++G** level.

[c] At the HF/6-311++G** level.

Table 4

NBO *donor/acceptor and the stable interacting energy* (*E*) *at the* B3LYP/6-311++G** *level* [a]

Donor [b]	Acceptor [c]	*E* (kJ/mol)	Donor [b]	Acceptor [c]	*E* (kJ/mol)
ANPyO			ANPy		
O_7	$C_{4'}$—$H_{14'}$	12.26	$N_{14'}$—$O_{15'}$	N_{17}—H_{19}	3.98
$N_{11'}$—$O_{13'}$	N_8—H_9	2.51	$N_{10'}$—$O_{12'}$	N_7—H_8	3.98
$N_{15'}$—$O_{16'}$	N_{18}—H_{20}	2.51	$O_{15'}$	N_{17}—H_{19}	12.52
$O_{13'}$	N_8—H_9	8.58	$O_{12'}$	N_7—H_8	12.52
$O_{16'}$	N_{18}—H_{20}	8.62	$N_{14'}$—$O_{15'}$	N_{17}—H_{19}	3.35
$N_{11'}$—$O_{13'}$	N_8—H_9	2.13	$N_{10'}$—$O_{12'}$	N_7—H_8	3.35
$N_{15'}$—$O_{16'}$	N_{18}—H_{20}	2.13			

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[a] Only those larger than 2 kJ/mol were listed, Atom numbering with a prime belongs to another submolecule.

[b] Donors are bonds or lone pairs.

[c] Acceptors are antibonds.

on the neighboring N—H bond are in the range of 0.026—0.048 with the exception of $N_1\cdots H_{13'}$, which reveals that there are H-bonds in the dimers. Compared to the HF method, the B3LYP method generates a slightly larger electron density of intermolecular bonding, but a smaller electron density of the covalent bond. There is hardly any interaction between $N_1\cdots H_{13'}$ due to its inaccessible long distance. Judging by the electron densities at the bond critical points, the individual O···H strength is stronger in the ANPy dimer than that in ANPyO, which is consistent with the O···H distance. As pointed out above, further approach of two submolecules is restricted in the ANPyO dimer by the deformation energy of the submolecule.

Natural bond orbital analysis. Table 4 lists the NBO analysis of the donor and acceptor (bond-antibond) between the submolecules and their stabilization energy ΔE btained by second order perturbation theory [11, 12]. This was carried out by examining all possible interactions between filled (donor) Lewis-type NBOs and empty (acceptor) non-Lewis NBOs; the stabilization energies ΔE are proportional to the NBO interacting intensities. When the donor and the acceptor belong to different submolecules in a dimer, we call it the intermolecular NBO interaction. It is the intermolecular NBO interaction that reveals the origin of intermolecular interactions. From Table 4, we can see that the *N*-oxide oxygen atom of the ANPyO dimer donates its lone pair to the neighboring C—H antibonds, which strengthens the intermolecular O···H interactions. The *N*-oxide oxygen atom as an electron donor (or H-bond acceptor) provides more stable interaction than nitro oxygen as a donor, with much more stabilization energy than the latter. Obviously, the O···H—C type of the H-bond is stronger in the ANPyO dimer than the ordinary O···H—C bond due to the *N*-oxide oxygen atom bearing larger negative charges with the resonance structure of $N^+ \rightarrow O^-$(NBO charges: –0.66 e for the oxygen atom). The largest NBO stabilization energy is 12.26 kJ/mol in the ANPyO dimer, which is consistent with the electron density values at the hydrogen bond critical points. The nitro oxygen atoms of the ANPy dimer donate their lone pairs to the neighboring N—H antibonds, which strengthens the intermolecular O···H interactions. The largest NBO stabilization energy in the ANPy dimer is 12.52 kJ/mol. Judging by the stabilization energy, the interaction between nitro oxygen and amino hydrogen is stronger in the ANPy dimer than that in the ANPyO dimer.

CONCLUSIONS

We can draw some conclusions from the first-principle calculations:

1. DFT-B3LYP method is not suitable for the systems with both C—H and N—H as H-bond donors.

2. The O···H—C-type of the H-bond is stronger in the ANPyO dimer than the ordinary one. However, the H-bond between the nitro and amino groups is weaker in ANPyO than the ordinary one.

3. The oxygen atoms donate lone pairs to the neighboring N—H or C—H antibonds. The stable energies are proportional to the NBO interacting intensities. The most stable interacting energy is 12.52 kJ/mol in the ANPy dimer.

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