

A Comparative Study of the DFT and MP2 Methods on Molecular Structure of Diphosphadithiatetrazocine

Gyusung Chung[†] and Duckhwan Lee^{*}

[†]Department of Chemistry, Konyang University, Nonsan, Chungnam 320-711, Korea

Department of Chemistry, Sogang University, Seoul 121-742, Korea

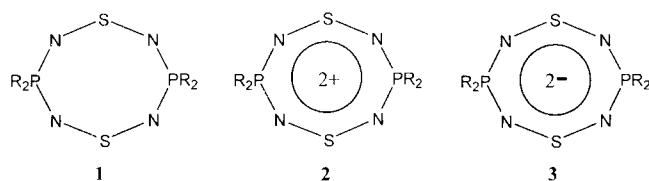
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The B3LYP method based on the density functional theory (DFT) is shown to be much better than the ab initio MP2 method for structural determination of diphosphadithiatetrazocine systems having transannular S---S bonding. The presence of bonding between the two sulfur atoms across the cyclic ring is theoretically confirmed in the case of the neutral diphosphadithiatetrazocine. The S---S bonding disappears in the ionized species. The planarity of the dicationic heterocyclic ring system turns out to be closely associated with the π -electron delocalization over the entire ring as well as the N-S-N bonds, which become stiffened upon ionization. In the case of dianionic species, the chair-boat and chair conformers are nearly degenerate and far more stable than the crown conformer.

Introduction

The density functional theory (DFT) method² is becoming a powerful computational tool for studying the structural properties of complex molecules. Because of its dramatic savings in computational effort, the DFT can be easily applied to large molecular systems. Furthermore, the DFT has been shown to be as accurate as or even better than the second-order Moeller-Plesset (MP2) calculations in many cases.³⁻⁵ Nevertheless, it has been reported that the DFT has difficulty in estimating the bond distances between the atoms interacting weakly through hydrogen bonding⁶ and van der Waals interaction.^{7,8} It is for such reason that the DFT method must be tested extensively before it can be applied with confidence to an entirely new class of molecular systems.

1,5-Diphosphadithiatetrazocines (1,5-R₄P₂N₄S₂), in which P-N and S-N units alternate in an eight-membered cyclic framework,⁹⁻¹⁶ are evidently a good molecular system for a comparative study of the DFT and MP2 methods since they are known to have unique transannular bonding between the two sulfur atoms. In addition, this molecular system is known to exhibit some interesting structural features, which require extensive theoretical investigation. Three kinds of 1,5-R₄P₂N₄S₂ system, **1**, **2**, and **3**, are considered to be interesting on this regard. The neutral¹⁰⁻¹³ and dicationic¹⁴ species, **1** and **2**, have been structurally characterized in detail while the structure of the 12 π -electron dianionic species **3**, though thermally stable, has not been fully analyzed.^{15,16}



According to the experimental results,^{10,11,13} the neutral species **1** has a folded structure along the S---S axis with the

planar N-P-N units on both sides of the transannular S---S axis. The short S---S distance of 2.50-2.55 Å determined by X-ray diffraction indicates the presence of unique transannular bonding between the two sulfur atoms. At the same time, the NMR study^{11,13} revealed the inequivalence of the *endo*- and *exo*-positions at the phosphorus atoms, which implies that the folded structure is reasonably rigid. It is also known that the heterocyclic ring takes on the planar geometry if R's are extremely bulky.¹⁴

The 8 π -electron dicationic species **2** with R=Et or Ph were isolated and characterized for the first time by Brock *et al.*¹⁴ Unlike the neutral species, the dicationic heterocyclic ring turns out to have planar structure. Since Et or Ph is too small to cause significant steric effect on the structure of the eight-membered ring system, it was not so evident how the dication takes on the planar geometry. It was furthermore pointed out by Brock *et al.* that the delocalization of π -electrons around the entire ring appears to be less likely since the S-N distance is shortened upon ionization to the extent that is typical for a localized Z,Z sulfur diimide (-N=S=N-) group while the P-N distance is increased from the neutral ring.¹⁴

It is the purpose of this paper to report a comparative study of the DFT and the ab initio MP2 computational methods on the unique heterocyclic system, which may have rare transannular S---S bonding. Molecular and electronic structures of the neutral, dicationic, and dianionic ring species will be investigated by using the B3LYP method⁷⁻¹⁹ based on the DFT methodology and the ab initio MP2 method. The utility of the DFT methodology in the case of molecular system having transannular S---S bonding will be verified and compared with the MP2 method. In addition, the structural features of the ring systems, especially the nature of the transannular S---S bonding and the planarity of the dicationic ring, will be analyzed in terms of the electronic structure obtained theoretically. The structure of the dianionic species as well as the relative stability of the substituted structural isomers of the neutral species will also be analyzed.

Computational Methods

The molecular geometries were fully optimized at the B3LYP and MP2 levels of the theory with the standard 6-31+G(d) basis set. For the neutral species, computations with the extended basis sets of 6-311+G(d) and 6-31+G(3df) as well as the MP4/6-31+G(d) calculation were also carried out. The MP2/6-31+G(d) hessian calculation was used to confirm whether or not the stationary points are indeed local minima.

For computational simplicity, a model compound with R=H was employed for analysis. The relative stabilities of the structural isomers of $[\text{RRP}]_2\text{N}_4\text{S}_2$ (R'=CCl₄, R=Cl) were also investigated at the B3LYP and the MP2 levels. The GAMESS²⁰ electronic structure program was used for all MP2 calculations, while the Gaussian 94¹ was used for the B3LYP and MP4 calculations.

Results and Discussion

B3LYP vs. MP2. The geometrical parameters obtained for the molecular systems depicted in Figures 1, 2, and 3 are summarized in Tables 1, 2, and 3, respectively. It is pointed out that the experimental values in Tables 1 and 2 are the X-ray data obtained from the molecular systems with R=Et or Me.

Except the neutral 1,5-H₄P₂N₄S₂ case, the geometrical parameters obtained from the B3LYP and MP2 calculations with the standard basis set agree quite well, within a few percents, with the experimental values as well as with each other. On the other hand, the B3LYP and MP2 methods result in significant disagreements for the neutral species. Especially, neither of the S---S distances of the two computational results agree with the experimental value.

Since the DFT is known to fail for molecular system hav-

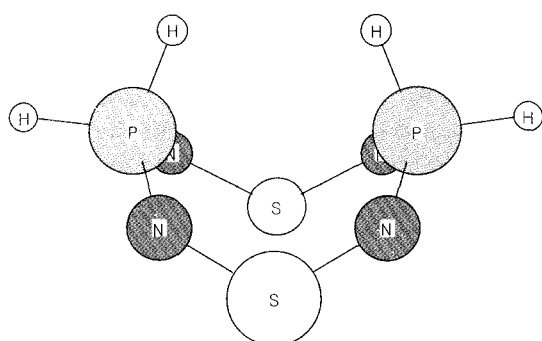


Figure 1. Molecular structure of neutral H₄P₂N₄S₂.

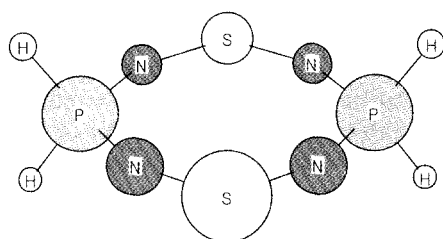


Figure 2. Molecular structure of dicationic H₄P₂N₄S₂.

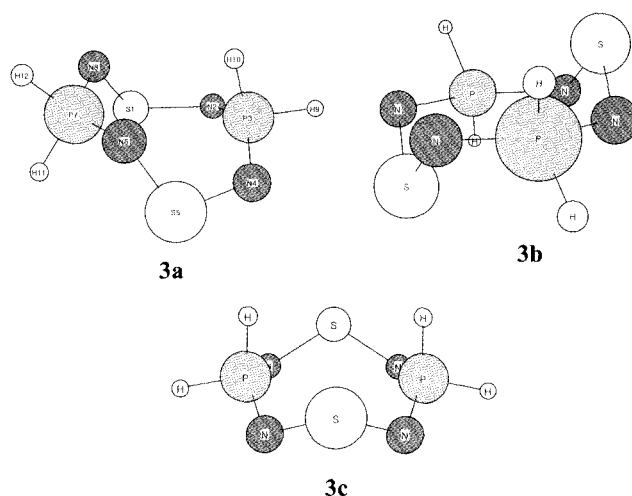


Figure 3. Molecular structures for possible conformers of dianionic H₄P₂N₄S₂, **3a** (chair-boat), **3b** (chair), and **3c** (crown).

ing weak hydrogen bonding⁶ or van der Waals interactions,^{7,8} it is quite tempting to regard the 10 π -electron 1,5-H₄P₂N₄S₂ system as yet another example of such failure of the DFT methodology since it may have rare transannular S---S bonding with the experimental distance of 2.551 Å. In this case, however, the S---S distance from the MP2/6-31+G(d) result of 3.200 Å is too far off to be acceptable.

In order to resolve the problem, the basis set dependency of the B3LYP and MP2 calculations was investigated. Although the S---S distance does not change much with the triple zeta split valence basis set, it turns out to be very sensitive to the addition of higher angular momentum basis functions. The S---S distance is drastically shortened by 0.32 Å in the MP2 calculation with the 6-31+G(3df) basis set, nearly twice the change in the B3LYP result.

It is necessary at this point to emphasize the fact that the two computational results agree quite well with each other (and with experiments) when the S---S distance is clearly out of the range of forming transannular bonding as in the dicationic and dianionic species as shown in Tables 2 and 3. Thus, it is quite certain that the disagreements between the two computational results are closely related to the formation of the transannular S---S bonding.

It is also noted that the B3LYP results with the standard basis set are in good agreement with the more extensive MP4 calculations, which are also presented also in Table 1. Thus, it appears to be reasonable to conclude that the B3LYP method based on the DFT is far more successful than the MP2 method for dealing with transannular S---S bonding. It is clearly demonstrated in this study that the higher angular momentum basis functions are necessary for the MP2 method in order to take into account the transannular S---S bonding character correctly.

Structure of the neutral and dicationic ring systems.

The neutral heterocyclic ring system indeed has the rigid structure folded along the two transannular sulfur atoms. The transannular S---S bond turns out to be quite strong with the bond order of 0.7. The molecular orbital responsible for

Table 1. Geometrical parameters of neutral $\text{H}_4\text{P}_2\text{N}_4\text{S}_2$, **1** (Distance, Å; Angles, deg)

Basis set	B3LYP			MP2		MP4		Expt ^a
	6-31+G(d)	6-311+G(d)	6-31+G(3df)	6-31+G(d)	6-311+G(d)	6-31+G(3df)	6-31+G(d)	
R(S-N)	1.625	1.616	1.601	1.629	1.619	1.602	1.619	1.595
R(P-N)	1.638	1.631	1.618	1.643	1.632	1.624	1.638	1.636
R(S---S)	2.866	2.873	2.668	3.200	3.206	2.879	2.750	2.551
$\angle\text{NSN}$	116.2	115.8	115.3	116.6	115.9	115.6	115.5	114.9
$\angle\text{PNS}$	121.8	123.3	121.0	123.9	125.2	121.3	120.4	120.7
$\angle\text{NPN}$	113.3	113.0	112.5	115.5	115.2	113.4	111.9	110.0

^afrom the x-ray structure of $\text{Me}_4\text{P}_2\text{N}_4\text{S}_2$; reference 10**Table 2.** Geometrical parameters of dicationic $\text{H}_4\text{P}_2\text{N}_4\text{S}_2$, **2** (Distance, Å; Angles, deg)

	B3LYP ^a	MP2 ^a	Expt. ^b
R(S-N)	1.540	1.553	1.510
R(P-N)	1.649	1.656	1.645
R(S---S)	4.426	4.430	
$\angle\text{NSN}$	119.1	120.2	121.6
$\angle\text{PNS}$	150.2	149.4	150.4
$\angle\text{NPN}$	150.2	121.0	117.6

^awith standard 6-31+G(d) basis set. ^bmean value of x-ray structure for $\text{Et}_4\text{P}_2\text{N}_4\text{S}_2^{2+}$ from reference 14.**Table 3.** Geometrical parameters of dianionic $\text{H}_4\text{P}_2\text{N}_4\text{S}_2$, **3a** and **3b**^a (Distance, Å; Angles, deg)

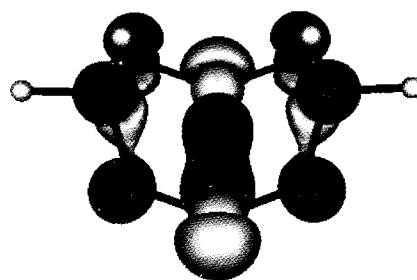
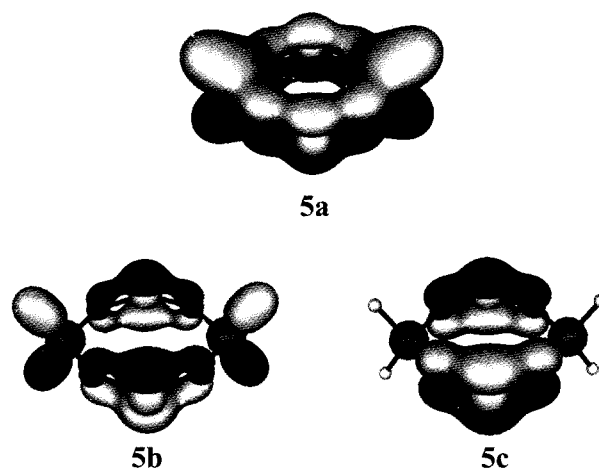
	3a		3b	
	B3LYP	MP2	B3LYP	MP2
R(S ₁ -N ₂)	1.737	1.727	1.736	1.726
R(S ₁ -N ₈)	1.750	1.741	1.736	1.726
R(P ₃ -N ₂)	1.634	1.637	1.638	1.639
R(P ₇ -N ₆)	1.641	1.643	1.638	1.639
R(S---S)	4.047	3.997	4.033	4.002
$\angle\text{NSN}$	111.7	110.2	106.6	105.2
$\angle\text{P}_3\text{N}_4\text{S}_5$	120.8	118.8	118.3	117.4
$\angle\text{P}_7\text{N}_6\text{S}_5$	113.9	112.9	118.3	117.4
$\angle\text{N}_2\text{P}_3\text{N}_4$	132.8	132.7	130.5	130.0
$\angle\text{N}_6\text{P}_7\text{N}_8$	128.4	128.9	130.5	130.0

^aatomic numberings as in Figure 3a and with 6-31+G(d) basis set.

such bonding is presented in Figure 4. The N-S and N-P bonds are of the single bond in their bonding character.

As for the dicationic ring system, it has not been clearly explained how the planar ring structure is achieved even in the absence of the steric effect arising from the bulky substituents at the phosphorus atoms. It was suggested by Brockel *al.* that the delocalization of the p-electrons along the planar ring may not be plausible since the electrons should be localized within the Z,Z sulfur diimide (-N=S=N-) bonds with the P-N distance increased upon ionization.¹⁴

The MP2 hessian calculation indicates that the planar structure indeed corresponds to a local minimum in the potential energy surface. The S---S distance of the dicationic ring system is over 4.4 Å, which is too large to form transannular bonding. It is however found that there exists a b_{1u} low-lying

**Figure 4.** Molecular orbital for transannular S---S bonding in the neutral $\text{H}_4\text{P}_2\text{N}_4\text{S}_2$.**Figure 5.** Occupied π -molecular orbitals of the dicationic $\text{H}_4\text{P}_2\text{N}_4\text{S}_2$ at the MP2/6-31+G(d). **5a**: fully delocalized π - b_{1u} (HOMO-0.257 hartree), **5b**: mixed b_{1u} (HOMO-0.138 hartree), **5c**: localized π - b_{3g} (HOMO-0.179 hartree)

occupied π -orbital, shown in Figure 5a, which is strongly delocalized over the entire ring system. At the same time, there are two occupied orbitals, depicted in Figures 5b and 5c, having the b_{1u} and b_{3g} , respectively, which seem to favor the planar ring structure. The b_{3g} orbital in Figure 5c is purely π -type concentrated around the N-S-N bonds while the b_{1u} orbital in Figure 5b has partial contributions from the P-H bonds. Due to the presence of these orbitals, the S-N bonding is strengthened to the bond order of 1.3 upon ionization. The bond order of N-P bond is about 0.8 in this dicationic ring. It is observed that the pure π -orbitals become unstable as the ring system is folded along the S-S axis while the mixed b_{1u} orbital is stabilized slightly. It is also noted that

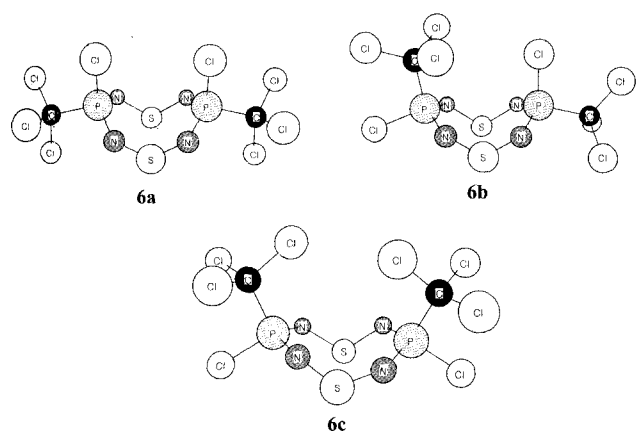


Figure 6. Molecular structure of $[R'RP]_2N_4S_2$ ($R=Cl$, $R'=CCl_3$). **6a** (endo-Cl, endo-Cl), **6b** (exo-Cl, endo-Cl) and **6c** (exo-Cl, exo-Cl)

Table 4. Geometrical parameters of 1,5-[(exo-CCl₃, endo-Cl)P]₂N₄S₂, **4a** (Distance, Å; Angles, deg)

	B3LYP ^a	MP2 ^a	Expt. ^b
R(S-N)	1.621	1.624	1.592
R(P-N)	1.616	1.614	1.607
R(S---S)	2.787	3.189	2.525
R(P-Cl)	2.050	2.022	1.982
R(P-C)	1.905	1.876	1.854
∠NSN	114.8	115.8	113.0
∠PNS	123.6	127.4	118.6
∠NPN	113.8	117.0	113.2

^awith 6-31+G(d) basis set. ^bmean values from reference 13

the P-N bond is strengthened at the expense of the S-N bonding in the dianionic heterocyclic system, which again has a puckered structure. Thus, it appears that the stronger S-N bonds with partial double bond character along with the fully delocalized b_{1u} π -orbital are the underlying reason for the planar structure of the dicationic heterocyclic ring system.

The relative stability of the neutral $[RRP]_2N_4S_2$ ($R=Cl$ and $R'=CCl_3$) system was also investigated at the B3LYP and MP2 levels of theory. There are three structural isomers, depicted in Figures **6a**, **6b** and **6c**, depending on the relative orientation of R and R' bonded to the phosphorus atoms. The RHF/6-31+G* hessian calculations show that all isomers are at the stationary point without imaginary frequency. Once again, the B3LYP results appear to be more successful than the MP2 calculations, especially with respect to the S---S distances. As expected intuitively, the structure **6a**, having two bulky trichloromethyl groups at the *exo* positions, turns out to be the most stable. The isomers **6b** and **6c** are 5.6 kcal/mol and 9.0 kcal/mol, respectively, higher in energy according to the B3LYP calculations. Once again, the B3LYP geometrical parameters as summarized in Table 4 are in better agreement with the experiments than the MP2 results.

Structure of the dianionic ring system. Although the dianionic ring system is known to be thermally stable, its structure has not been fully clarified experimentally. Indeed, the calculations result in several possible conformers, chair-

boat, chair and crown, as shown in Figure 3, each of which corresponds to different local minimum on the MP2 potential energy surface. It was not possible to find the local minimum corresponding to the boat-boat conformer. The chair-boat and chair conformers, which are nearly degenerate, are far more stable than the crown conformer, by more than 45 kcal/mol. The chair conformer is more stable by about 1.0 kcal/mol in the B3LYP calculations, while the chair-boat form is more stable by about 0.8 kcal/mol in the MP2 calculations.

A good agreement between the B3LYP and MP2 calculations was again achieved as far as the geometrical parameters obtained for the two stable conformers. As noted before, the P-N bond is strengthened to the bond order of 1.4 at the expense of the S-N bond whose bond order decreases to 0.6. Nevertheless the P-N distance does not change much compared with the neutral and dicationic species. It is also interesting to note that the S---S distance is about the same as the sum of the van der Waals radii of two sulfur atoms, indicating that the transannular bonding may begin to appear in this dianionic ring system.

Conclusions

The B3LYP calculation based on the density functional theory turns out to be as good as or even better than the MP2 method for structural analysis of the neutral, dicationic and dianionic $P_2N_4S_2$ ring systems. The B3LYP method is especially successful, even comparable to the far more extensive MP4 calculations, for the molecular system having transannular S---S bonding. It is noted that the higher angular momentum basis functions must be supplemented to the MP2 calculations for such cases.

The transannular S---S bonding in the 10π -electron neutral system is clearly confirmed through theoretical calculations. The S---S distance in the dianionic ring system is about the same as the sum of the van der Waals radii of two sulfur atoms. Such bonding disappears completely in the dicationic system as the S---S distance increases significantly to over 4 Å. It is however observed that the π -orbital which is fully delocalized over the entire ring seem to be responsible, along with stronger S-N bonds, for the planar structure of the dicationic system. It is shown in the case of dianionic ring system that two stable conformers are nearly degenerate in energy.

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