Isomers of P_2S_2

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To help future structural characterization of gaseous P_2S_2 by experimental techniques, accurate relative energies, geometries, rotational, and quartic centrifugal distortion constants, dipole moments, harmonic vibrational frequencies, infrared intensities, and vertical ionization energies have been determined from *ab initio* calculations for several isomers of P_2S_2. There are at least five minima identified on the lowest singlet potential energy surface of P_2S_2. The energy results obtained indicate that a PP-bridged bicyclic (butterfly-type) isomer of C_{2v} symmetry corresponds to the global minimum, while the planar cyclic 4-membered isomers of D_{2h} and C_{2v} symmetries are the second and third most stable isomers, respectively.

I. Introduction

Small, volatile phosphorous oxides received considerable attention in recent years from experimentalists and theoreticians alike.[1−15] While the large and stable P_4O_6 and P_4O_{10} phosphorous oxides are well known, several of the smaller P_xO_y ($x = 1-4$, $y = 1-5$) species have only recently been characterized in matrix isolation studies[1−9] and by observing the related rotational signals using millimeterwave spectroscopy.[10] Quantum chemical calculations of varying sophistication have been performed to explore the rich structural chemistry and to help in the experimental identification of these short-lived species.[10−15] As expected, several interesting structures have been observed including cyclic, bridge-bonded, and cagelike forms, many of which are completely uncharacteristic of the formal first-row N_xO_y ground electronic state analogs. The structural investigations[16−20] of small sulfur oxides revealed similarly unusual structural motifs, proving once again that the structural trends for molecules containing second-row atoms are rather dissimilar to the (formal) first-row analogs. Similar structural curiosities have been observed for sulfur−nitrogen compounds[21−25] as well as in small carbon−analog silicon compounds[26,27] and many other species involving second-row atoms.[28]

Purely second-row compounds received less attention. For example, apart from a recent matrix infrared study of Andrews and co-workers,[29] no information seems to be available for nonsolid phosphorous sulfides P_xS_y with $2 < x + y < 7$. Even *ab initio* calculations are scarce. It was therefore decided to carry out a systematic *ab initio* investigation of all possible structural isomers of P_2S_2, a formal analog of N_2O_2,[30−32] N_2S_2,[21−25] and P_2O_2.[11,13,15] While N_2O_2 is relatively well-characterized,[30−32] only very limited amount of experimental structural information is known about the N_2S_2 and P_2O_2 isomers. *Ab initio* calculations,[15] after some confusion,[11,12] settled in favor of a cyclic D_{2h} symmetry isomer as the lowest-energy form on the potential energy surface (PES) of P_2O_2. It seems also well-established in the literature that a D_{2h}-symmetry ring is the global minimum for N_2S_2.[21−25]

During the course of this study structural characterization of several isomers of P_2S_2 was attempted using a wide range of methods of molecular electronic structure theory. The calculations were aimed, for example, to determine the isomer that corresponds to the global minimum on the lowest singlet PES of P_2S_2 and what are the relative energy estimates of the stationary points determined. The results obtained are of intrinsic interest and, furthermore, past experience suggests that high-level structural results from these *ab initio* calculations should prove most valuable for future structural characterization of the several isomers of P_2S_2. Another aim of this study was the examination of the nature of bonding in certain P_2S_2 isomers, especially in view of recent interest in the study of multiple bonds involving second-row elements.[28]

II. Computational Details

Several basis sets have been selected for this study. The smaller ones are the 3-21G* [33] and the 6-31G* basis sets,[34] which were employed in a number of earlier theoretical studies on compounds containing phosphorus and sulfur. They have been employed to allow comparison of results obtained in the present study with earlier ones. The correlation-consistent, polarized-valance cc-pVTZ basis of Dunning and co-workers[35] has been extensively employed in calculations aiming at results of considerably higher accuracy. In some calculations, the TZP and TZ2P basis of Ahlrichs et al.[36] have also been used. The compact 3-21G*(6-31G*), the TZP, the TZ2P, and the cc-pVTZ basis sets contain 76, 108, 128, and 136 CGF's for P_2S_2, respectively. The d and f sets of the TZP, TZ2P, and cc-pVTZ basis sets included only the five and seven pure spherical harmonics, while in the case of the 3-21G* and 6-31G* sets, as usual, the six Cartesian d functions have been employed.

Electronic wave functions were determined by the single configuration, self-consistent field, restricted Hartree−Fock (RHF) method,[37−39] by second-, third-, and fourth-order Møller−Plesset[40] theory, i.e. MP2, MP3, and MP4(SDTQ), by coupled cluster (CC) methods including all single and double excitations (CCSD) and in cases, additionally, a perturbative correction for contributions from connected triple excitations (CCSD(T)),[41−44] and by a hybrid density functional (DFT) approach usually abbreviated as B3LYP.[45] The T_1 diagnostic values of coupled cluster theory[44c,d] are around 0.02 for the different structures of P_2S_2 investigated, suggesting that at least the ground electronic states of these isomers can adequately be described by single-reference-based electron correlation methods. The 1s, 2s, and 2p core orbitals have been kept frozen in all MP*n* and CC treatments, except the TZP CCSD and TZ2P CCSD(T) geometry optimizations, i.e., the 20 molecular orbitals of lowest energy have been kept doubly occupied.

The geometrical structures of the isomers of P_2S_2 were optimized at the 3-21G* RHF, 6-31G* MP2, cc-pVTZ RHF and DFT(B3LYP), TZP CCSD, and TZ2P CCSD(T) levels of theory. The residual Cartesian gradients were in all cases less

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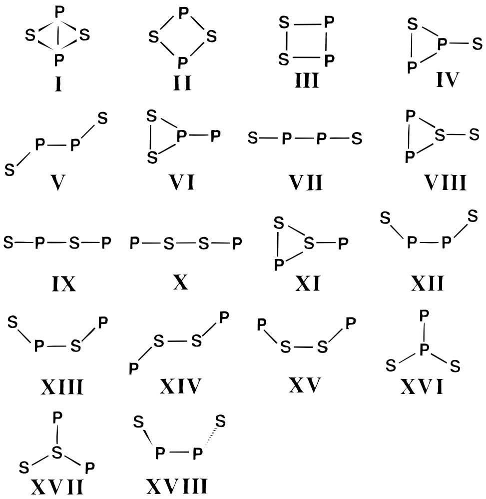

Figure 1. Structures of P_2S_2 investigated in this study.

than 1×10^{-4} Hartree/Bohr. For all optimized structures, except the ones obtained at the CCSD and CCSD(T) levels, the Cartesian quadratic force fields were determined at the respective optimized geometries, employing analytic second derivative techniques.

For accurate determination of vertical ionization energies (VIE) the equation-of-motion-ionization-potential (EOMIP)-CCSD method,[46,47] a special version of EOM-CCSD,[48] has been employed.

The electronic structure computations were performed with the program packages GAUSSIAN94[49] and ACESII.[50] For the calculation of most molecular constants the package ASYM20 was employed.[51]

III. Results and Discussion

With a little imagination approximately 20 structures can be drawn for P_2S_2, as seen on Figure 1. Numbering of the lower-energy structures is based upon their energy order from cc-pVTZ RHF and DFT(B3LYP) geometry optimizations: the larger the structure number the higher its relative energy. Naturally, many of these structures are just lower-symmetry analogs of higher-symmetry ones but they should nevertheless be treated as distinct during the course of a systematic *ab initio* investigation.

The possible stationary points on the potential energy surface (PES) of P_2S_2 belong to four distinct categories: sequentially bonded, branched, 3-membered-ring, and 4-membered-ring structures. The two possible planar 4-membered-ring structures, **II** and **III** of D_{2h} and C_{2v} symmetries, respectively, proved to be minima at all levels of theory employed. While the nonplanar PP-bridged bicyclic isomer, **I**, quickly collapsed to **II** upon optimization at the 3-21G* RHF level of theory, it proved to be the global minimum at all higher levels of theory. Note that for P_2O_2 a PP-bridged bicyclic (“butterfly”) isomer was also located[12] as a minimum at the 6-31G* RHF level of theory, although it did not prove to be the global minimum. The two C_{2v}-symmetry 3-membered-ring isomers proved to be minima at all levels of theory, as well; thus, their nonplanar analogs were not investigated. From the two C_s-symmetry 3-membered-ring structures, **IV** and **XI**, **IV** turned out to have the lower energy. Optimization of structure **XI** failed both at the 6-31G* MP2 and cc-pVTZ B3LYP levels due to ring opening, while the RHF-optimized minima have two extremely low frequencies. Therefore, **XI** is considered not to be existent on the lowest singlet PES of P_2S_2.

The branched structures, **XVI** and **XVII** of Figure 1, are very similar to the 3-membered rings but they contain only three bonds originating from the central atom. All investigated planar and nonplanar branched structures collapsed to 3-membered-ring isomers upon geometry optimization.

The most structural variations could have been expected for the sequantially bonded structures. Point-group symmetry of these structures can be as high as C_{2h} and as low as C_1. Structure **VII**, SPPS, is of lowest energy of the possible linear forms. It has a high energy if compared to isomer **I** and does not correspond to a minimum. No planar *cis* or *trans* forms of lower than C_{2v} or C_{2h} symmetry, respectively, could be located at either the RHF or MP2 levels. For example, *cis*-SPSP, **XIII**, collapsed to the second most stable isomer **II**, while *cis*-PSSP, **XV**, to **III**. While *trans*-SPPS, **V**, of C_{2h} symmetry could be located as a stationary point at all levels, it never proved to be a minimum. Optimization of *trans*-PSSP, **XIV**, never resulted in a stationary point with an SS bond length less than 2.7 Å; as a rule, structures with an extremely weak bond formed between two PS molecules were excluded from further consideration. Allowing the atoms to move out of the plane resulted in no stable structures. In summary, it seems that no sequentially bonded or branched structures correspond to minima on the lowest singlet PES of P_2S_2.

Table 1 contains energy results from geometry optimizations performed at the RHF, DFT(B3LYP), MP2, CCSD, and CCSD(T) levels of theory. Table 2 contains energy estimates from high-level single-point MP*n* and coupled-cluster calculations employing cc-pVTZ B3LYP reference geometries. Molecular constants of various isomers are listed in Table 3. Geometry parameters of these isomers are given in Table 4, while, for purposes of comparison, theoretical and experimental bond lengths of the ground electronic states of the P_2, S_2, and PS molecules are listed in Table 5. Vibrational frequencies and infrared intensities of various P_2S_2 isomers are given in Table 6. Vertical ionization energies of the four most stable P_2S_2 isomers, obtained from cc-pVTZ EOM-CCSD computations, are collected in Table 7. Table 8 contains relative energy estimates of various P_2O_2 and N_2S_2 isomers, formal analogs of P_2S_2. Finally, Table 9 summarizes atomic net charges of some P_2S_2 isomers. In general, important structural aspects of the isomers are highlighted but no exhaustive discussion of all features for all isomers is given.

III.1. Relative Energies. The detailed *ab initio* calculations employed revealed the following minima on the lowest singlet PES of P_2S_2: **I**, **II**, **III**, **IV**, **VI**, and perhaps **VIII**. As Table 1 shows, all stationary points found but the first three have so high relative energies that their experimental observation seems somewhat unlikely. The dimerization energy 2 PS ($X^2\Pi$) → **I** is calculated to be 15 730 cm^{-1} at the cc-pVTZ B3LYP level of theory. Although this value might be somewhat uncertain, it clearly indicates that isomers **I**−**IV** are bound with respect to two PS molecules. Results from higher-level calculations, presented in Table 2, reveal that once reasonably large basis sets are used, electron correlation beyond MP2 plays usually a rather small part in the relative energy predictions. It can also be seen, from comparison of entries in Tables 1 and 2, that the hybrid DFT functional B3LYP produces reliable relative energy predictions. Therefore, large basis set MP2 and DFT(B3LYP) calculations should prove indispensable for *ab initio* electronic structure calculations on related (and larger) inorganic systems.

Ab initio geometry optimizations, except the one at the 3-21G* RHF level, as well as single-point energy calculations performed with extended basis sets (TZP, TZ2P, and cc-pVTZ) prefer the bridged-bonded isomer **I** over the planar 4-membered

TABLE 1: Relative Energies (in cm^{-1}) of Various P_2S_2 Structures Obtained from *ab Initio* Geometry Optimizations[a]

		RHF					
isomer	sym	3-21G*	cc-pVTZ	MP2 6-31G*	B3LYP cc-pVTZ	CCSD TZP	CCSD(T) TZ2P
I	C_{2v}	0 [0][b]	0 [0]	0 [0]	0 [0]	0	0
II	D_{2h}	−1 470 [0]	4 870 [0]	620 [0]	1 800 [0]	2 940	1 960
III	C_{2v}	−2 070 [0]	4 170 [0]	4 090 [0]	3 670 [0]	4 110	3 860
IV	C_s	5 100 [0]	11 180 [0]	10 140 [0]	10 000 [0]	11 840	
V	C_{2h}	12 750 [1]	20 730 [1]	10 430 [0]	12 750 [1]		
VI	C_{2v}	12 860 [0]	19 320 [0]	10 630 [0]	17 430 [0]	18 400	
VII	$D_{\infty h}$	20 440 [2]	27 150 [2]	18 580 [2]	24 370 [2]		
VIII	C_{2v}	36 100 [1]	39 860 [1]	30 630 [0]	31 160 [0]		
IX	$C_{\infty v}$	48 240 [2]	52 680 [2]	37 030 [2]	—[c]		
X	$D_{\infty h}$	73 060 [2]	75 840 [2][e]	—[c]			
XI	C_s	32 310 [0][d]	37 180 [0][f]	—	—		

[a] The relative energy values are taken with respect to the total energy of **I**, determined to be −1469.500 434, −1476.627 459, −1476.895 075, −1479.254 753, −1477.572 725, and −1477.696 873 au at the 3-21G* RHF, cc-pVTZ RHF, 6-31G* MP2, cc-pVTZ DFT(B3LYP), TZP CCSD, and TZ2P CCSD(T) levels of theory, respectively. sym = Point group symmetry of the structure. For each structure the number of imaginary frequencies at any given level of theory are given in square brackets. [b] C_2-Symmetry-optimized structure, **XVIII**, the original PP-bridged C_{2v} structure collapsed to **II** at this level of theory. [c] No stationary point was found with a central bond length less than 2.5 Å. This choice excludes isomers with an extremely weak bond formed between two PS molecules from further consideration. [d] The lowest two nonzero frequencies are only 140 and 46 cm^{-1}. [e] Two more frequencies of 4 cm^{-1}. [f] The lowest two nonzero frequencies are only 172 and 112 cm^{-1}.

TABLE 2: Relative Energies (in cm^{-1}) of Various P_2S_2 Isomers from Single-Point Energy Calculations[a]

isomer	RHF	MP2	MP4	CCSD	CCSD(T)	T_1[b]
I	0	0	0	0	0	0.019
II	5 070	1 080	1 660	3 220	2 330	0.015
III	4 250	5 070	4 340	4 420	4 260	0.020
IV	11 260					
VI	19 450	18 760	18 870	18 450	18 010	0.022
VIII	40 290	31 220	14 220	35 000	32 550	0.022

[a] Energies were calculated at the respective cc-pVTZ B3LYP-optimized geometries. The MP2, MP4, CCSD, and CCSD(T) relative energy values are taken with respect to the total energy of **I**, determined to be −1476.625 816, −1477.259 996, −1477.262 381, −1477.288 386, and −1477.333 114 au at the cc-pVTZ RHF, MP2, MP4, CCSD, and CCSD(T) levels, respectively. [b] The T_1 diagnostic values of coupled cluster theory.[44c]

rings and clearly establish it as the global minimum on the lowest singlet PES of P_2S_2. At all levels of theory the planar 4-membered-ring isomers are among the isomers of lowest relative energy, as can be seen in Tables 1 and 2. While all correlated-level calculations (including B3LYP) predict the highly symmetric **II** to be more stable, the introductory 3-21G* RHF calculations prefer **III** by a small amount. This problem is not associated with the use of the limited 3-21G* basis, as cc-pVTZ RHF calculations also prefer **III** by a similar amount, about 800 cm^{-1}. One would expect that single-reference methods had problems describing **II** due to its possible biradical character. It is perhaps in line with this expectation that RHF theory is unable to predict the greater stability of **II** over **III**. Note also that the largest CCSD amplitude for **II** is large, 0.146, and, as expected, corresponds to the HOMO−LUMO excitation. This large amplitude value should be kept in mind when the low T_1 diagnostic value of **II** is considered. (For comparison, the largest amplitude for **I** is only 0.044). Then it must be emphasized that all single-reference electron correlation methods yield relative energies of similar magnitude and thus suggest that proper description of **II** can be achieved by these methods. Perhaps further support for this view is provided by the lack of extremely low frequency fundamentals for **II** at the different theoretical levels (cf. Table 6 below), since the appearance of fundamentals of too low frequency indicate that the structure may not be described correctly by a single-determinant wave function.

III.2. Structures and Rotational Spectra. In recent years (sub)millimeter wave (rotational) spectroscopy turned out to be a leading source for structural information on metastable and short-lived species.[52] In order to successfully search for rotational signals of any of the P_2S_2 isomers, a more or less accurate knowledge of the rotational and quartic centrifugal distortion (QCD) constants, as well as the size of the dipole moment components of the isomers, is needed. Therefore, these data are presented in Table 3 for five isomers of P_2S_2.

The most stable P_2S_2 isomer, **I**, has a sizeable dipole moment, it is 0.9 D at the TZ2P CCSD(T) level. Thus, this isomer should be amenable to detection by millimeter wave spectroscopy. Unfortunately, the second most stable P_2S_2 isomer, **II**, has no permanent dipole moment, thus it will be difficult to observe it by rotational spectroscopy. The dipole moment of **III** is quite small at all levels of theory, it is only 0.03 D at the TZ2P CCSD(T) level, raising fears that observation of this isomer might prove to be difficult, as well.

It is clear from Table 3 that the cc-pVTZ B3LYP rotational constants are rather close the their TZP CCSD and TZ2P CCSD(T) counterparts, the three sets of numbers should have comparable accuracy. This is encouraging for future application of DFT theory for structural studies of second-row species. The reported QCD constants, obtained from cc-pVTZ RHF computations, are expected to be rather accurate. In line with previous studies,[27,53] they might be some 12% too low.

Since only isomers **I**−**IV** are serious contenders for future experimental characterization, structural parameters are reported only for them in Table 4.

The prototype P═P double bond length in P_2 is 1.8934 Å,[54] while it is calculated to be 1.8952 Å at the cc-pVTZ B3LYP level and about 1.91 Å at most other levels of theory (for detailed results see Table 5). The PP single bond in P_4 has a length of 2.21 Å, as determined from electron diffraction measurements[55] and from an analysis of the rovibrational Raman spectrum.[56] Note that a detailed analysis of the calculated bond lengths in P_2 and P_4 has recently been published by Häser and Trautler,[57] who concluded that very large basis sets and explicit consideration of core-valence correlation effects are needed to obtain a consistent theoretical P═P bond length close to the experimental equilibrium value, while the single bond length in P_4 is easily predicted from frozen-core calculations. The S═S double bond length in S_2 is 1.889 Å, while the typical S−S single bond length is 2.061 Å in H_2S_2.[58] It is interesting to note that the S_2 bond length is calculated to be substantially longer than the P_2 bond length at all levels of theory but cc-pVTZ CCSD(T), in contrast with the well-established experimental trend.

TABLE 3: Molecular Constants of Isomers of P_2S_2[a]

isomer	level	A_e	B_e	C_e	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K	μ_{tot}
I	RHF	4772.9	2741.5	2350.0	0.346	0.158	1.120	0.023	0.322	0.96
	MP2	4733.0	2704.4	2307.4						
	B3LYP	4665.5	2637.7	2263.3						0.94
	CCSD	4629.7	2651.9	2270.6						1.11
	CCSD(T)	4561.6	2611.8	2240.6						0.94
II	RHF	3854.9	3731.2	1896.0	0.563	−1.180	1.855	0.240	−0.007	0.00
	MP2	3746.6	3550.6	1823.0						0.00
	B3LYP	3672.0	3618.4	1822.5						0.00
	CCSD	3709.0	3594.2	1825.4						0.00
	CCSD(T)	3614.9	3561.8	1794.0						0.00
III	RHF	3818.7	3645.3	1865.0	0.379	0.896	−0.659	0.147	0.736	0.26
	MP2	3676.2	3616.9	1823.1						
	B3LYP	3678.2	3556.5	1808.2						0.06
	CCSD	3668.9	3554.0	1805.4						0.20
	CCSD(T)	3612.8	3512.7	1781.1						0.03
IV	RHF	5725.6	1941.7	1449.9	0.128	1.305	5.324	0.039	1.071	0.94
	MP2	5525.5	1887.3	1406.8						
	B3LYP	5469.3	1885.2	1402.0						0.91
	CCSD	5525.8	1874.6	1399.7						1.02
VI	RHF	6742.1	1787.7	1413.0						1.05
	MP2	6368.2	1754.7	1375.7						
	B3LYP	6424.3	1730.2	1363.1						0.72
	CCSD	6387.7	1727.4	1359.6						0.36

[a] The RHF, MP2, DFT(B3LYP), CCSD, and CCSD(T) values are results from the respective cc-pVTZ RHF, 6-31G* MP2, cc-pVTZ B3LYP, TZP CCSD, and TZ2P CCSD(T) geometry optimizations. Rotational constants (A_e, B_e, C_e) are given in megahertz, quartic centrifugal distortion (QCD) constants (Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K) in kilohertz. All QCD constants refer to the *A*-reduced representation.

TABLE 4: Geometry Parameters of Isomers of P_2S_2[a]

isomer	parameter	cc-pVTZ RHF	cc-pVTZ B3LYP	TZP CCSD	TZ2P CCSD(T)
I	r(PS)	2.143	2.178	2.176	2.194
	r(PP)	2.100	2.126	2.135	2.147
	∠SPS	90.0	90.6	90.1	90.1
II	r(PS)	2.058	2.099	2.098	2.116
	∠SPS	88.2	88.7	88.2	88.7
III	r(PP)	2.033	2.089	2.082	2.104
	r(SS)	2.067	2.090	2.102	2.112
	r(PS)	2.099	2.125	2.126	2.138
	∠SPP	90.5	90.0	90.3	90.1
IV[b]	r(PP)	1.973	2.007	2.005	
	$r(P_hS)$	2.007	2.046	2.051	
	r(PS)	2.368	2.422	2.409	
	$r(P_tS)$	1.885	1.912	1.915	
	$\angle PP_hS_t$	73.0	73.4	72.9	
VI	r(SS)	2.165	2.218	2.225	
	r(PP)	1.891	1.919	1.929	
	r(PS)	2.051	2.092	2.089	
	∠SPS	63.7	64.0	64.3	

[a] Bond lengths, *r*, in angstroms, bond angles, ∠, in degrees. For numbering of the atoms see Figure 1. [b] Lower index t indicates the terminal S atom, while P_h the P atom connected to it.

TABLE 5: Equilibrium Bond Lengths (*r*/Å), in the Ground Electronic States of P_2, S_2, and PS[a]

method	$r(P_2)$	$r(S_2)$	r(PS)
cc-pVTZ RHF	1.8571	1.8695	1.8790
cc-pVTZ B3LYP	1.8952	1.9135	1.9115
TZP CCSD	1.9110	1.9203	1.9211
TZ2P CCSD(T)	1.9218	1.9305	1.9321
cc-pVTZ CCSD(T)	1.9119_3	1.9118_7	1.9184
expt[b]	1.8934	1.889	$[1.900_9]$

[a] Restricted reference functions in all cases, except for the B3LYP calculations on $X^3\Sigma_g^-$ S_2 and $X^2\Pi$ PS, where an unrestricted formalism has been employed. All electrons have been correlated in the coupled-cluster calculations. [b] Reference 54.

The calculated PP bond length of **I**, 2.17 Å, is much longer than 1.9 Å, the prototype P═P double bond length, it is even longer than *r*(PP) in **III**. Thus, it is a somewhat weakened single bond emphasizing the trivalent nature of bonding around P in **I**. The high symmetry of **II** requires all SP bonds to have the same length. It is noteworthy that the bond angle at P in this isomer is slightly less than 90° at all levels of theory. The SS bond length of **III**, 2.07 Å, is characteristic of a S−S single bond. The generally poor multiple bonding ability of second-row atoms suggests that the formally P═P double bond in **III** is closer to a single bond which is supported by the calculated bond length. An interesting curiosity of the shape of **III** is that it is an almost perfect rectangle; for example, the SSP bond angle is 89.99° at the cc-pVTZ B3LYP level, while the PP and SS bond lengths differ by only 0.001 Å, both being shorter than the SP bonds. Comparison of the theoretical P_2 and S_2 bond lengths reported in Table 5 with experiment suggests that if **III** is ever observed, its SS bond length might be shorter than its PP bond length. Isomer **IV** is characterized by a PP bond length somewhat shorter than the typical single bond values and by a terminal PS bond which is not only short but also highly polarized (P^+S^-), so that it could be easily characterized by infrared spectroscopy.

III.3. Vibrational Spectra. The plethora of information contained in the cc-pVTZ RHF, 6-31G* MP2, and cc-pVTZ B3LYP theoretical vibrational frequencies and infrared intensities presented in Table 6 for the P_2S_2 isomers would allow interpretation of a carefully executed matrix isolation infrared investigation. Due to the lack of experimental data no elaborate scaling, like the one resulting in a scaled quantum mechanical (SQM) force field,[59] is attempted here.

The most intense, and at the same time the only strong, feature in the predicted IR spectrum of **I** is around 470 cm^{-1}, a b_1 symmetry fundamental properly called ν_5. Unfortunately, **II** has its most intense band of b_{1u} symmetry in the same region of the spectrum, at the cc-pVTZ B3LYP level the difference at the predicted values is only 2 cm^{-1}. This fact should prove valuable during identification of P_2S_2, but might hinder identification of the individual isomers. The terminal PS bond of **IV** is short and highly polarized, resulting in the strongest vibrational absorption in any of the P_2S_2 isomers in a region where the appearance of a strong band is unique among isomers **I**−**IV**.

III.4. Vertical Ionization Energies. Photoelectron spectroscopy and its several variants (e.g., ZEKE spectroscopy[60])

TABLE 6: Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) of P_2S_2 Isomers[a]

isomer[b]	level	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ΔZPVE
I	RHF	677(6)	537(62)	489(14)	417(4)	361(0)	297(1)	0
	MP2	630(4)	494(47)	462(11)	387(3)	308(0)	278(2)	0
	B3LYP	608(4)	465(55)	447(9)	371(4)	273(0)	262(0)	0
II	RHF	609(0)	608(0)	521(35)	458(43)	388(0)	260(1)	+32
	MP2	597(104)	551(0)	525(0)	492(13)	334(0)	224(1)	+82
	B3LYP	538(0)	531(0)	467(19)	462(0)	328(0)	235(1)	+66
III	RHF	668(0)	591(22)	538(20)	492(7)	374(1)	228(0)	+56
	MP2	575(11)	534(15)	493(5)	484(0)	323(1)	202(0)	+26
	B3LYP	538(0)	531(0)	467(19)	462(0)	328(0)	235(1)	+62
IV	RHF	897(252)	581(46)	536(10)	283(1)	223(2)	209(1)	−24
	MP2	893(84)	576(32)	494(10)	263(4)	197(1)	143(0)	+4
	B3LYP	832(130)	534(28)	482(8)	257(2)	185(0)	184(1)	+23
VI	RHF	879(100)	560(5)	459(21)	403(21)	195(0)	141(1)	−103
	MP2	843(129)	486(9)	407(30)	358(17)	173(0)	154(0)	−151
	B3LYP	805(88)	490(4)	380(24)	358(20)	168(0)	142(0)	−109

[a] The RHF, MP2, and DFT(B3LYP) frequencies were determined, using the cc-pVTZ, 6-31G*, and cc-pVTZ basis sets, respectively, at the respective optimized geometries. The vibrational fundamentals of the isomers are reported simply in descending order. ΔZPVE = relative zero-point vibrational energy correction with respect to the ZPVE of **I**. [b] See Figure 1.

TABLE 7: Vertical Ionization Energies (in cm^{-1}) of the Four Most Stable P_2S_2 Isomers[a]

	I			**II**			**III**			**IV**		
order	EOMIP	Koopmans	sym	EOMIP	Koopmans	sym	EOMIP	Koopmans	sym	EOMIP	Koopmans	sym
$\tilde{X}$	73 310	78 840	b_2	66 310	62 990	b_{1g}	73 250	72 430	b_1	67 700	69 780	a''
$\tilde{A}$	73 860	76 790	a_1	80 980	84 500	b_{2u}	75 730	79 740	a_2	79 370	83 770	a'
$\tilde{B}$	82 090	83 590	b_1	81 720	84 940	b_{2g}	81 100	85 100	a_1	82 810	88 280	a''
$\tilde{C}$	93 270	98 020	a_1	88 150	93 720	b_{1u}	83 130	87 140	b_2	91 470	93 050	a'
$\tilde{D}$	97 880	101 920	a_2	97 700	110 620	b_{3u}	100 720	111 450	b_1	99 220	106 570	a'
$\tilde{E}$	102 340	108 150	b_2	101 440	110 390	a_g	105 830	113 730	a_1	101 210	109 920	a''

[a] EOMIP = EOMIP-CCSD. sym = Symmetry of the cationic state. All values reported were obtained with the cc-pVTZ basis set.

could possibly be used to detect isomers of P_2S_2. Theory can aid these experimental investigations by determining ionization energies, E_i, which, among other things, determine the appearance of the related spectra. While theoretical determination of adiabatic ionization energies is costly, modern molecular electronic structure theory provides efficient methods for the prediction of vertical ionization energies (VIEs). The most cost-effective method is the equation-of-motion ionization potential coupled-cluster singles and doubles (EOMIP-CCSD) method,[46,47] which provides vertical E_i's in a single run. In this sense its usefulness is similar to that of Koopmans' theorem; however, applications[46,47,61,62] revealed that, unlike Koopmans' theorem, EOMIP-CCSD can produce VIE's accurate to better than 0.5 eV. To show how different the two predictions are for higher cationic excited states (higher ionization energies), both sets of E_i's are presented in Table 7 for the four most stable P_2S_2 isomers. It is interesting to note in this respect that as expected, all E_i's but the first ones for **II** and **III** are calculated to be considerably smaller using EOMIP-CCSD. More importantly, Koopmans' theorem predicts the correct order of the VIE's for all isomers but **I**, where it predicts $\tilde{A}$ to be smaller than $\tilde{X}$.

The theoretical data reveal that there should be substantial differences in the photoelectron spectra of the different P_2S_2 isomers, allowing relatively easy identification of them. The small difference in the first two ionization energies of **I** is due to the symmetric and antisymmetric combinations of lone pairs, while the 7000 cm^{-1} lowering of the first ionization energy of **II** as compared to **I** is due to delocalization effects. Finally, it is noted that although **IV** has a similar first ionization energy as **II**, the much larger abundance of **II** should ensure that it dominates the relevant region of the photoelectron spectrum of P_2S_2.

III.5. Bonding Features. Failure of the calculations employing the 3-21G* basis set to properly describe the isomers of P_2S_2 could have far-reaching consequences, as this basis set has been used extensively in the past to study similar compounds, including the related molecules N_2S_2 and P_2O_2. Note also that, as far as one can judge from the published reports, C_2-symmetry chain-like structures, like **XVIII**, have not been considered during earlier theoretical treatments of the isomers of P_2O_2 and N_2S_2. Therefore, cc-pVTZ B3LYP geometry optimizations followed by cc-pVTZ MP4(SDTQ) and CCSD(T) single-point energy calculations have been performed for these molecules of intrinsic interest for this study. The results obtained for three isomers of P_2O_2 and N_2S_2, having the same structures as **I**−**III** of P_2S_2, are collected in Table 8. These calculations support earlier studies for both P_2O_2 and N_2S_2 in that the C_2-symmetry structures are not minima but collapse to "butterfly" structures. The most important conclusion of these calculations, however, is that the bicyclic structures are the global minima neither for P_2O_2 nor for N_2S_2. For P_2O_2 the bicyclic isomer is some 4000 cm^{-1} higher in energy than the global minimum D_{2h} structure, while the planar C_{2v} structure is much higher in energy. For N_2S_2 the situation is less clear. It seems from the present calculations that the planar C_{2v} structure is the global minimum, although the MPn (n = 2, 3, 4) results show the D_{2h} structure to be the global minimum. Therefore, one can conclude that (a) P_2S_2 is unique in this series in the sense that its global minimum is a PP-bridged butterfly structure; (b) the PP bridge is much stronger than the SS bridge; and (c) participation of the d orbitals of S in the bonds stabilizes the butterfly structure in P_2S_2.

The central PP linkage in **I** shows a single-bound character, as can be expected from pairing of the unpaired electrons of the PS fragments and evidenced from the PP bond length. The D_{2h}-symmetry isomer **II** can be classified as a π-electron-rich compound since it has six π electrons distributed over four centers. As expected, the Mulliken population analysis shows a negligible P−P overlap population for **II**. Since **II** can be classified as an electron-rich system and it possesses a relatively

TABLE 8: Relative Energies (in cm^{-1}) of Various P_2O_2 and N_2S_2 Isomers from *ab Initio* Calculations[a]

molecule	isomer	B3LYP	RHF	MP2	MP4	CCSD	CCSD(T)	T_1[b]
P_2O_2	**I**	0	0	0	0	0	0	0.023
	II	−3 800	−1 270	−4 920	−4 340	−3 280	−4 010	0.015
	III	23 380	21 690	22 180	24 820	20 480	20 140	0.025
N_2S_2	**I**	0	0	0	0	0	0	0.019
	II	−15 110	−16 010	−17 130	−15 130	−14 450	−14 300	0.015
	III	−17 470	−21 330	−13 800	−14 580	−16 720	−15 780	0.023

[a] Energies were calculated at the respective cc-pVTZ B3LYP optimized geometries, for which energy results are collected in the third column. The MP2, MP4, CCSD, and CCSD(T) relative energy values are taken with respect to the total electronic energies of isomers **I**, determined to be −831.252 741 (−903.823 219), −832.014 427 (−904.601 277), −832.072 253 (−904.667 918). −832.018 934 (−904.603 248), and −832.061 380 (−904.654 628) au at the cc-pVTZ RHF, MP2, MP4, CCSD, and CCSD(T) levels, respectively, for P_2O_2(N_2S_2). Numbering of the isomers follows that applied for P_2S_2. [b] The T_1 diagnostic values of coupled cluster theory.[44c]

TABLE 9: Atomic Net Charges (*q*) of P_2S_2 Isomers[a]

isomer	parameter	cc-pVTZ RHF	TZP CCSD	TZ2P CCSD(T)
I	q(P)	+0.23	+0.19	+0.19
II	q(P)	+0.10	+0.13	+0.16
III	q(P)	+0.07	+0.06	+0.06
IV	$q(S_t)$	−0.27		
	$q(P_h)$	+0.51		
	q(S)	−0.22		
VI	$q(P_t)$	−0.17	−0.07	
	$q(P_h)$	+0.37	+0.27	
	q(S)	−0.10	−0.10	

[a] Obtained from Mulliken population analysis.[63]

small HOMO-LUMO gap, it is expected to exhibit Hartree−Fock instability similar to that observed in N_2S_2,[22] where an instability was triggered by a modest increase of r(SN) from its equilibrium value. Investigation of this possible instability is not pursued here.

Table 9 summarizes the atomic net charges computed using the population analysis method of Mulliken.[63] The diatomic molecule PS has a dipole moment of ≈0.8 D with a polarization of P^+S^- and charges of ≈0.1. The atomic charges assigned to the P_2S_2 isomers compare with those of diatomic PS. The large positive charge of the bridgehead P atom in isomers **IV** and **VI** is noteworthy; the large PP and PS charge separations in these isomers explain the large intensities of their corresponding stretching vibrations.

IV. Conclusions

The large amount of high-level *ab initio* data presented in this study provides vital data for different types of experiments applicable to probe P_2S_2. In particular, the following conclusions can be drawn about the shape and spectra of the P_2S_2 isomers and about their determination by experimental techniques and by methods of electronic structure theory:

(1) The lowest-energy isomer on the lowest singlet PES of P_2S_2 is a nonplanar PP-bridged bicyclic ("butterfly") compound of C_{2v} symmetry. Note that the bicyclic structure is not the global minimum for the related molecules P_2O_2 and N_2S_2. Planar cyclic P_2S_2 of D_{2h} symmetry, **II**, is the second most stable isomer at all except the lowest levels of theory. No sequentially bonded structure seems to correspond to a minimum on the singlet planar potential energy hypersurface of P_2S_2.

(2) The introductory 3-21G* RHF level of theory fails to predict the relative stabilities of the lowest-energy isomers and predict minima which prove to be false at higher levels of theory. Therefore, use of the compact 3-21G* RHF method cannot be recommended for future studies on phosphorus and sulfur compounds.

(3) In line with previous theoretical studies the calculated cc-pVTZ RHF rotational and quartic centrifugal distortion (QCD) constants are expected to be of high quality and thus should help future identification of all P_2S_2 isomers but **II** by rotational spectroscopy.

(4) The calculated vibrational spectra of the isomers of P_2S_2 reveal that different isomers have some high-intensity bands in different regions of the spectrum. These differences in the normal modes would probably allow identification of a number of isomers in the low-temperature inert gas matrix vibrational spectrum of P_2S_2.

(5) Vertical ionization energies calculated using the EOMIP-CCSD method reveal that there should be substantial differences in the photoelectron spectra of the different P_2S_2 isomers allowing relatively easy identification of them.

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References and Notes

(1) Ngo, T. A.; DaPaz, M.; Coquart, B.; Couet, C. *Can. J. Phys.* **1974**, *52*, 154.

(2) (a) Kawaguchi, K.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1983**, *79*, 629. (b) Kawaguchi, K.; Saito, S.; Hirota, E.; Ohashi, N. *J. Chem. Phys.* **1985**, *82*, 4893.

(3) (a) Andrews, L.; Withnall, R. *J. Am. Chem. Soc.* **1988**, *110*, 5606. (b) Withnall, R.; Andrews, L. *J. Phys. Chem.* **1988**, *92*, 4610. (c) Withnall, R.; McCluskey, M.; Andrews, L. *J. Phys. Chem.* **1989**, *93*, 126. (d) Mielke, Z.; McCluskey, M.; Andrews, L. *Chem. Phys. Lett.* **1990**, *165*, 146.

(4) Kanata, H.; Yamamoto, S.; Saito, S. *J. Mol. Spectrosc.* **1988**, *131*, 89.

(5) Qian, H. B.; Hamilton, P. A.; Davies, P. B. Unpublished results.

(6) Hamilton, P. A. *J. Chem. Phys.* **1987**, *86*, 33.

(7) Ghosh, S. N.; Verma, R. D. *J. Mol. Spectrosc.* **1978**, *72*, 200.

(8) Larzilliere, M.; Jacox, M. E. *J. Mol. Spectrosc.* **1980**, *79*, 132.

(9) Verma, R. D.; McCarthy, C. F. *Can. J. Phys.* **1983**, *61*, 1149.

(10) Bailleux, S.; Bogey, M.; Császár, A. G.; Demuynck, C.; Destombes, J. L.; Dujardin, N.; Liu, Y.; Davies, P. B. Unpublished results.

(11) Lohr, L. L. *J. Phys. Chem.* **1990**, *94*, 1807.

(12) Lohr, L. L. *J. Phys. Chem.* **1992**, *96*, 119.

(13) Davy, R. D.; Xie, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1991**, *113*, 3697.

(14) Bruna, P. J.; Mühlhäuser, M.; Peyerimhoff, S. D. *Chem. Phys. Lett.* **1991**, *180*, 606.

(15) Lopez, X.; Sarasola, C.; Lecea, B.; Largo, A.; Barrientos, C.; Ugalde, J. M. *J. Phys. Chem.* **1993**, *97*, 4078.

(16) Marsden, C. J.; Smith, B. J. *Chem. Phys.* **1990**, *141*, 325.

(17) Marsden, C. J.; Smith, B. J. *Chem. Phys.* **1990**, *141*, 335.

(18) Lovas, F. J.; Tiemann, E.; Johnson, D. R. *J. Chem. Phys.* **1974**, *60*, 5005.

(19) Harcourt, R. D. *J. Am. Chem. Soc.* **1980**, *100*, 5195.

(20) Harcourt, R. D. *J. Mol. Struct.* **1989**, *186*, 131.

(21) MacDiarmid, A. G.; Mikulski, C. M.; Russo, P. J.; Saran, M. S.; Garito, A. F.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 476.

(22) Laidlaw, W. G.; Benard, M. *J. Comput. Chem.* **1987**, *8*, 727.

(23) Findlay, R. H.; Palmer, M. H.; Downs, A. J.; Edgell, R. G.; Evans, R. *Inorg. Chem.* **1980**, *19*, 1307.

(24) Karpfen, A.; Schuster, P.; Petkow, J.; Lischka, H. *J. Chem. Phys.* **1978**, *68*, 3884.

(25) Warn, J. R.; Chapman, D. *Spectrochim. Acta* **1966**, *22*, 1371.

(26) Cordonnier, M.; Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Chem. Phys.* **1992**, *97*, 7984.

(27) Bogey, M.; Bolvin, H.; Cordonnier, M.; Demuynck, C.; Destombes, J. L.; Császár, A. G. *J. Chem. Phys.* **1994**, *100*, 8614.

(28) Cowley, A. H.; Norman, N. C. *Progr. Inorg. Chem.* **1986**, *34*, 1.

(29) Mielke, Z.; Brabson, G. D.; Andrews, L. *J. Phys. Chem.* **1991**, *95*, 75.

(30) Ewing, G. E. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 486.

(31) Skaarup, S.; Skancke, P. N.; Boggs, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6106.

(32) (a) Benzel, M. A.; Dykstra, C. E.; Vincent, M. A. *Chem. Phys. Lett.* **1981**, *78*, 139. (b) Ha, T.-K. *Theor. Chim. Acta* **1981**, *58*, 125. (c) Michels, H. H.; Montgomery, J. A. *J. Chem. Phys.* **1988**, *88*, 7248. (d) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F., III. *Theor. Chim. Acta* **1989**, *75*, 81.

(33) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(34) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(35) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(36) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(37) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69; **1960**, *32*, 179.

(38) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.

(39) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(40) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(41) Cizek, J. *J. Chem. Phys.* **1966**, *45*, 4256.

(42) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(43) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(44) (a) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *86*, 2881. (b) Scuseria, G. E.; Lee, T. J. *J. Chem. Phys.* **1990**, *93*, 5851. (c) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199. (d) Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer: Dordrecht, 1995; p 47.

(45) (a) Dirac, P. A. M. *Proc. Cambridge Philos. Soc.* **1930**, *26*, 376. (b) Becke, A. D. *Phys. Rev. B* **1988**, *38*, 3098. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (e) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(46) (a) Meissner, L.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *94*, 6670. (b) Stanton, J. F.; Gauss, J. *J. Chem. Phys.* **1994**, *101*, 8938.

(47) (a) Nooijen, M.; Snijders, J. G. *Int. J. Quantum Chem.* **1993**, *48*, 15. (b) Nooijen, M.; Snijders, J. G. *J. Chem. Phys.* **1995**, *102*, 1681.

(48) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 7029.

(49) Frisch, M. J., et al. Gaussian94, Revision B.2, Gaussian Inc.: Pittsburgh, PA, 1995.

(50) ACESII is an electronic structure program written by Stanton, J. F., Gauss, J., Watts, J. D., Lauderdale, W. J., Bartlett, R. J., Quantum Theory Project, University of Florida, 1991.

(51) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

(52) Hirota, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1.

(53) (a) Császár, A. G.; Fogarasi, G. *J. Chem. Phys.* **1988**, *89*, 7646. (b) Clabo, D. A.; Allen, W. D.; Remington, R. B.; Yamaguchi, Y.; Schaefer, H. F., III. *Chem. Phys.* **1988**, *123*, 187. (c) Császár, A. G. *Chem. Phys. Lett.* **1989**, *162*, 361. (d) Császár, A. G.; Fogarasi, G.; Boggs, J. E. *J. Phys. Chem.* **1989**, *93*, 7644. (e) Wlodarczak, G.; Burie, J.; Demaison, J.; Vormann, K.; Császár, A. G. *J. Mol. Spectrosc.* **1989**, *134*, 297. (f) Allen, W. D.; Yamaguchi, Y.; Császár, A. G.; Clabo, D. A., Jr.; Remington, R. B.; Schaefer, H. F., III. *Chem. Phys.* **1990**, *145*, 427.

(54) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, Vol. IV, Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.

(55) Maxwell, L. R.; Hendrichs, S. B.; Mosley, V. *J. Chem. Phys.* **1935**, *3*, 699.

(56) Brassington, N. J.; Edwards, H. G. M.; Long, D. A. *J. Raman Spectrosc.* **1981**, *11*, 346.

(57) Häser, M.; Treutler, O. *J. Chem. Phys.* **1995**, *102*, 3703.

(58) Marsden, C. J.; Smith, B. J. *J. Phys. Chem.* **1988**, *92*, 347.

(59) (a) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037. (b) Allen, W. D.; Császár, A. G.; Horner, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 6834.

(60) Müller-Dethlefs, K.; Schlag, E. W. *Annu. Rev. Phys. Chem.* **1991**, *42*, 109.

(61) (a) Sinha, D.; Mukhopadhyay, S. K.; Chaudhuri, R.; Mukherjee, D. *Chem. Phys. Lett.* **1989**, *154*, 544. (b) Mukhopadhyay, D.; Mukhopadhyay, S.; Chaudhuri, R.; Mukherjee, D. *Theor. Chim. Acta* **1991**, *80*, 441.

(62) Szalay, P. G.; Császár, A. G.; Nemes, L. *J. Chem. Phys.* **1996**, *105*, 1034.

(63) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833; 1841; 2338; 2343.