

Structure of 6π -Electron Four-Membered Rings Containing Second-Row Atoms

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An ab initio quantum chemical study is presented on 6π -electron four-membered $1,3-X_2Z_2Y_2Z'_2$ ($X = P, S$; $Y = C, N, O, P, S$; $Z, Z' = H$, lone pair) rings. Stationary points on the potential energy surfaces were fully optimized within the symmetry constraints using SCF/6-31G* and MP2/6-31G* methods and characterized by calculating the harmonic vibrational frequencies of the normal modes. It is shown that besides experimentally known 6π -electron four-membered rings (S_2N_2 , S_4^{2+}) several $1,3-X_2Z_2Y_2Z'_2$ rings possess a planar (aromatic) configuration. Alternatively, a distorted C_s structure or a puckered C_{2v} structure with a trans-annular bond are found. The theoretical geometric parameters are in good agreement with available X-ray crystallographic data on a number of these compounds, their derivatives, or their complexes with transition metals. The preference for a planar, distorted, or puckered structure is rationalized in terms of 1,3-repulsive interactions and stabilizing deformations of the planar rings.

Introduction

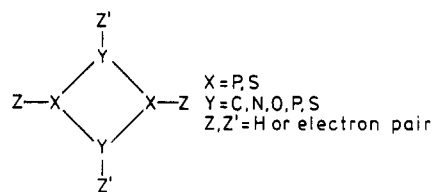
Aromaticity is one of the most important concepts in organic chemistry, explaining the structure, stability and reactivity of cyclic π -conjugated molecules.¹ Moreover, aromaticity provides a rationale for the course and stereochemistry of pericyclic reactions. Although challenged in recent years,² the $4n+2$ π -electron criterion, known as Hückel's rule, is fundamental in the description of the delocalization of π electrons and aromatic stabilization.

A notable exception to this simple electron-counting rule is the fact that organic 6π four-membered rings are unknown. The archetype cyclobutadiene dianion has been subject of ab initio calculations. Hess et al.³ have shown that despite 6π electrons the dianion of cyclobutadiene is unstable in a planar tetragonal conformation and distorts toward a nonplanar C_s arrangement as a result of electron localization and a tendency to minimize the overlap in its potential 6π system. Subsequent calculations by van Zandwijk et al.⁴ revealed that the cyclobutadiene dianion in fact favours a trapeziform carbon ring with the two hydrogen atoms on the long C-C bond out of plane in either a *syn* (C_s) or a *anti* (C_2) conformation. The negative charge in these structures is primarily confined to the carbon atoms forming the long bond. This suggests that electrophilic addition leads to a 1,2-disubstituted 3-cyclobutene, in agreement with the transient formation of the dianion claimed by McKennis et al.⁵ Budzelaar et al.⁶ studied two other examples of organic 6π four-membered rings, 1,3-diazetene ($C_2H_2N_2H_2$), and 1,3-dioxetene ($C_2H_2O_2$), and found for both that the planar conformation is unstable. The absence of aromaticity has been ascribed to strong repulsive 1,2- and/or 1,3-interactions in the higher occupied molecular orbitals and electronegativity differences in heterocyclic rings. More recently van Zandwijk et al. have shown that low-frequency out-of-plane vibrational modes of substituents on the ring are of major importance for the stability of these electron-rich 6π four-membered rings.⁴ 6π aromaticity in these rings depends on a fine balance of stabilizing and distortive properties which depend on the nature of the constituting atoms and the presence of ring substituents.

Although there is no principal remonstrance against extrapolating Hückel's rule to heterocyclic rings, a straightforward extension to inorganic rings is not evidenced by experimental or theoretical results. One of the most obvious examples in this respect is hexazine, the all-nitrogen analogue of benzene. At present positive identification of N_6 has not been achieved. The

structure of N_6 isomers has been subject of several recent computational investigations.^{7,8} High-level ab initio calculations have shown that in contrast to benzene, hexazine, N_6 , prefers a nonplanar twist-boat D_2 structure, whereas the D_{6h} alternative is a second-order saddle point.⁷ The most stable N_6 isomer was found to be a twisted open-chain C_2 structure, still well above the energy of three N_2 molecules. For the second-row analogue, P_6 , ab initio calculations show that the planar hexagon has the highest energy of all structural isomers, whereas the benzvalene and prismane structures have the lowest energies.⁹

In contrast to their organic analogues a limited number of 6π four-membered inorganic rings has been identified experimentally. Well-known examples are S_2N_2 , S_4^{2+} , Se_4^{2+} , and Te_4^{2+} which invariably contain second-row (or heavier) ring atoms.¹⁰ Given the fact that 6π electron six-membered inorganic rings are less stable than their organic analogues, it seems that this behavior is reversed for 6π four-membered rings. The question emerges, whether inorganic 6π electron four-membered rings, in general, are more stable than the corresponding organic rings. To answer this question, ab initio quantum chemical calculations are presented on a number of 6π four-membered rings containing phosphorus or sulfur with the following general structure:



Several derivatives of these $1,3-X_2Z_2Y_2Z'_2$ electron-rich rings are known experimentally, either as pure compounds or as ligands incorporated in transition-metal complexes. Their geometries range from a planar tetragon to nonplanar and strongly puckered conformations. The aim of this study is to reveal and account for the conformational preferences of these rings and to establish relevant candidates with aromatic character. It will be shown that, besides the planar conformation, a number of other stationary points on the potential energy surface can be located, of which some correspond to stable configurations. The various (local) minima on the potential energy surface are compared with X-ray crystallographic data when available. In general the agreement between experimental and theoretical geometric parameters is good. This gives confidence to the calculated geometries of species

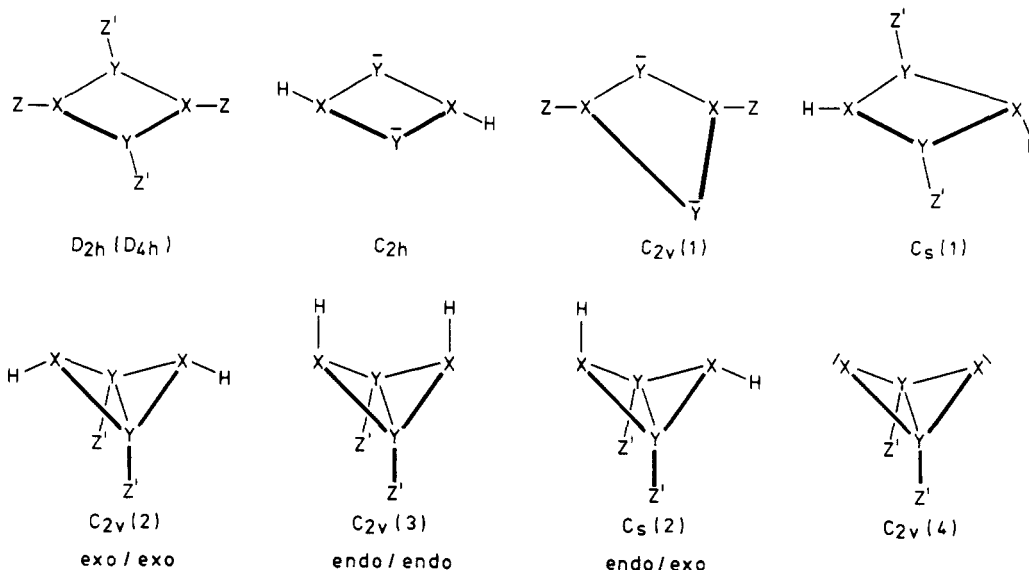


Figure 1. Definition of basic structural types of 1,3- $X_2Z_2Y_2Z'_2$ rings. ($X = P, S; Y = C, N, O, P, S; Z, Z' = H, \text{lone pair}$).

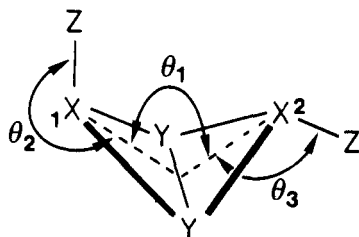


Figure 2. Definition of θ_1 , θ_2 , and θ_3 used for describing the geometry of puckered rings.

that have not been identified experimentally so far. It is demonstrated that several factors, viz. the presence of substituents, repulsive 1,2- and 1,3-interactions, and bond strength, contribute to the conformational preferences. Their consequences are explored in detail.

Method

Ab initio molecular orbital calculations were carried out with the GAMESS and GAUSSIAN90 systems of programs.^{11,12} All geometries were completely optimized at the closed-shell restricted Hartree-Fock (RHF) level using 3-21G and 6-31G* basis sets. For a number of local minima at the 6-31G* level improved geometries and energies were obtained by incorporating electron correlation using Møller-Plesset perturbation theory (MP2/6-31G*). The optimized geometries are subject only to overall molecular symmetry constraints. Although it is well-known that the 3-21G basis set is inadequate for an accurate description of the geometry and energy of compounds containing (hypervalent) second-row elements, this basis set was included in the calculations. Combining the 3-21G and 6-31G* results provides some means to assess the convergence of the calculations with respect to the theoretical level. The reported calculations, however, will focus on the SCF/6-31G* and MP2/6-31G* calculations. Significant differences between 3-21G and 6-31G* are explicitly indicated throughout the next section. Tables presenting detailed information on the SCF/3-21G calculations are included as supplementary material (see paragraph at end of paper).

To establish the various minima on the potential energy surface the following procedure was used. In a first step the molecule is optimized using the highest possible symmetry constraint (D_{2h}/D_{4h}) and the associated harmonic vibrational frequencies are analytically computed. Using the normal modes representing an imaginary frequency the symmetry break down of the molecule is found and a new point group is obtained. This results in most cases in the correct symmetry of a local minimum. Exceptions occur when new imaginary-frequency modes arise in a subsequent

geometry optimization or when stabilization of an imaginary-frequency mode takes place. For all optimized geometries a vibrational analysis was performed to find the order of the stationary point. In case a particular conformation possesses only real harmonic vibrational frequencies, no further attempts were made to establish minima of lower symmetry. The geometries of the bicyclobutane-like structures were computed in a gradient optimization starting from various initially puckered conformations corresponding to the $C_{2v}(2)$, $C_{2v}(3)$, $C_s(2)$, and $C_{2v}(4)$ principal structures (Figure 1). In every case the order of the stationary point obtained was determined.

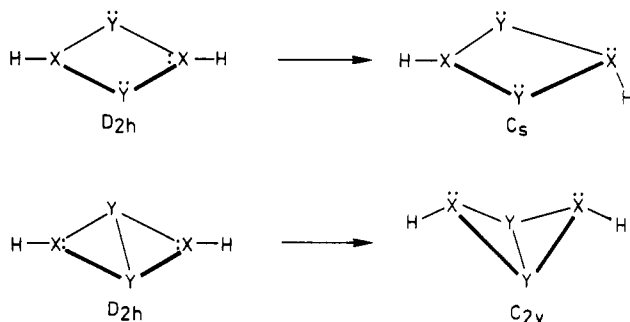
Results

The structure, stability and distortive properties of the 1,2- $X_2Z_2Y_2Z'_2$ systems were studied restricting the calculations to the following constraints: (i) six π electrons, (ii) only neutral or doubly charged species, and (iii) optionally hydrogen atoms are included as a substituent on the ring atoms. For compounds obeying these criteria a detailed analysis of the minima and stationary points on the potential energy surface is performed.

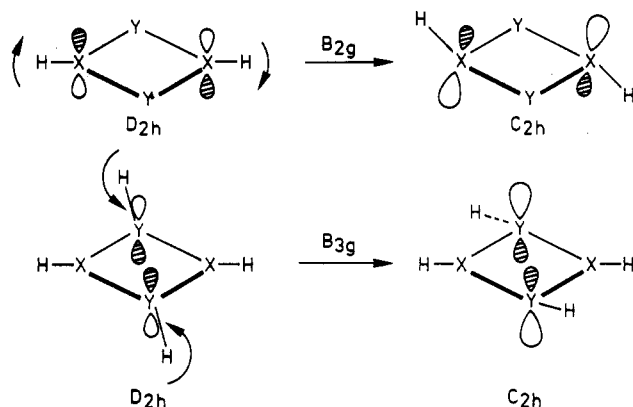
Total energies (SCF/6-31G* and MP2/6-31G*) and the order of the stationary points are collected in Table I. Results of the vibrational analysis of the D_{2h} and D_{4h} conformations are summarized in Table II. Geometry data on various optimized geometries are given in Table III (D_{2h} and D_{4h}), and Table IV (C_{2h} , C_s , and C_{2v}). The geometric parameters tabulated in Table IV are defined in Figure 2.

Before discussing the results on the individual compounds it is instructive to consider the general electronic structure of 6 π -electron four-membered rings in more detail. The principal Lewis structures of 6 π -electron four-membered 1,3- $X_2Z_2Y_2Z'_2$ rings ($Z, Z' = \text{free electron pair or substituent}$) depicted in Figure 3 clearly demonstrate their electron-rich character. As a consequence of the fact that there are more π electrons than atoms in the ring, it is not possible to present a single Lewis structure for a homonuclear ring ($X = Y$ and $Z = Z'$) in which all four nuclei are simultaneously equivalent. Any fully electron-delocalized (aromatic) structure must therefore consist of resonance between, at least, four equivalent structures. In principle five basic Lewis structures (I–V, Figure 3) can be envisaged, each of which possesses two or four equivalent configurations. Structures III and V incorporate expanded valence shell nuclei and formally require the inclusion of d orbitals as hybridization functions within the Lewis scheme. IV and V represent spin-paired diradical structures with a long or formal trans-annular bond. Whenever electron localization occurs, possibly as a consequence of an electronegativity difference between XZ and YZ' , it will be

associated with a reduction of the overall symmetry from D_{2h} (or D_{4h}). The resulting geometry will reflect the resonance structure that caused the deformation, e.g.:



Similar conclusions can be derived from an analysis of the π -molecular orbital scheme of a $1,3-X_2Z_2Y_2Z'_2$ ring (Figure 4).^{4,6} With 6π electrons the π_1 , π_2 , and π_3 molecular orbitals are completely filled. Since π_2 and π_3 are 1,2-nonbonding and 1,3-antibonding a trans-annular 1,3-repulsive interaction exists. The principal deformations observed for these rings can be attributed to the tendency of the rings to minimize the 1,3-repulsive interaction. Depending on the electronegativity difference between XZ and YZ' either a B_{2g} or B_{3g} deformation is favored:



It is important to note that these deformations only occur in case $Z = H$ (B_{2g}) and/or $Z' = H$ (B_{3g}). A third deformation which can result in stabilization is a B_{1u} pucker mode. In this case the energy-lowering is a result of populating π_4 in stead of π_3 . In contrast to π_3 , the π_4 MO is 1,3 bonding. Since puckering will increase the 1,3 overlap and decrease the 1,2-overlap, it lowers the MO energy of π_4 and simultaneously increases the energy of π_3 , resulting in a trans-annular bond (Figure 4). From our previous study on first-row 6π -electron four-membered rings,⁴ it appeared that an imaginary B_{1u} pucker mode for a D_{2h} ring occurs concurrently with an imaginary B_{2g} deformation. Superposition of the B_{2g} and B_{1u} deformation modes transforms a D_{2h} geometry into a C_s conformation:

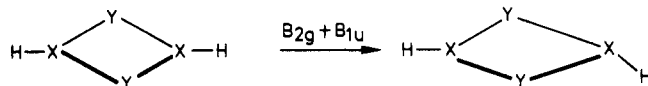


Figure 1 contains the various basic structural types encountered in this study, i.e., a planar structure, nonplanar distorted conformations, and strongly puckered butterfly-like bicyclo[1.1.0]-butane geometries. Starting from the D_{2h} geometry with the highest possible symmetry, three conformations of lower symmetry (C_{2h} , C_{2v} (1), and C_s (1)) can be obtained following a deformation along B_{2g} , B_{2u} , or $(B_{2g} + B_{1u})$ imaginary vibrational frequency modes. For the puckered rings with a trans-annular bridgehead bond in principle four different bicyclobutane-like conformations (C_{2v} (2), C_{2v} (3), C_s (2), and C_{2v} (4)) exist depending on the presence and orientation of hydrogen substituents. The first three

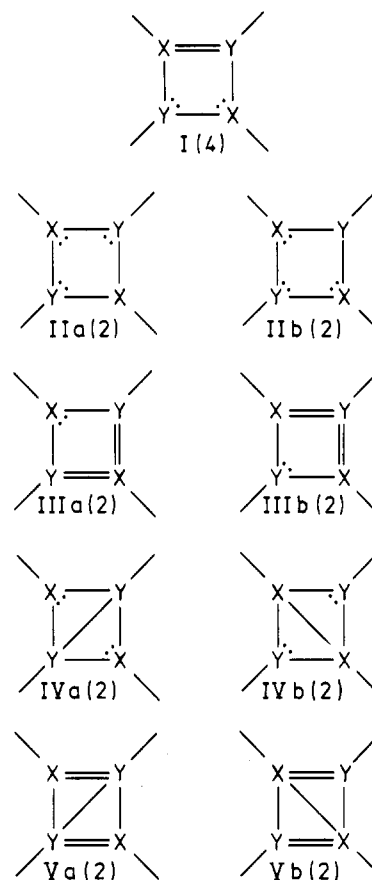


Figure 3. Principal Lewis structures of 6π -electron four-membered rings. The number of equivalent resonance configurations is given in parentheses.

structures differ by the orientation of the hydrogen atoms viz., exo/exo (C_{2v} (2)), endo/endo (C_{2v} (3)), and endo/exo (C_s (2)), whereas C_{2v} (4) possesses no hydrogen substituents on the non-bridgehead 1,3 positions.

1.1. Carbon-Phosphorus Rings (1–20). Four-membered rings with 6π electrons incorporating phosphorus and carbon in an alternating sequence are unknown as isolated substances. Derivatives of 1,3-diphosphacyclobutadiene (4π electrons) have been reported in organometallic complexes.¹³ X-ray crystallographic analysis of three different cobalt complexes with a η^4 -2,4-di-*tert*-butyl-1,3-diphosphabutadiene (η^4 -(*t*-BuCP)₂) ring: [Co(η^5 -Cp){ η^4 -(*t*-BuCP)₂}], with Cp = C₅H₅, [Co(C₉H₇){ η^4 -(*t*-BuCP)₂}], and [Co(η^5 -Cp*){ η^4 -(*t*-BuCP)₂}], with Cp* = C₅Me₅, reveal a planar ring conformation in which all four PC bond lengths are essentially equivalent and amount to 1.797, 1.796, and 1.805 Å, respectively.¹⁴ This indicates an electron-delocalized structure in the complexed form. The respective PCP angles are 98.9, 99.5, and 98.3°. As a result of complexation with the metal, the actual number of π -electrons in the ring is unknown. In fact these complexes can be considered as capped annulene rings for which a $4n+2$ interstitial electron rule, describing aromaticity in three dimensions, has been proposed.¹⁵

Calculations on the 1,3-diphosphete dianion 1 ($C_2H_2P_2^{2-}$) reveal that the D_{2h} optimized PC bond length depends to some extent on the theoretical level and varies from 1.772 to 1.791 Å (Table III). The MP2/6-31G* geometric parameters PC = 1.791 Å and PCP = 97.2° are in good agreement with the experimental data of the cobalt complexes.¹⁴ The negative charge in 1 is mainly localized on the carbon atoms. The diametric repulsive 1,3-interaction of the two phosphorus atoms results in an imaginary frequency for the gerade hydrogen out of plane vibration (B_{2g}) at all levels of theory. Subsequent optimization of the C_{2h} structure results in a stable geometry (2), slightly below the D_{2h} configuration (−1.5 kcal/mol at 6-31G*). At the 6-31G* level C_{2h} 2 is the global minimum. All four geometry-optimized bicyclobutane-like conformations (3–6) correspond to stable minima

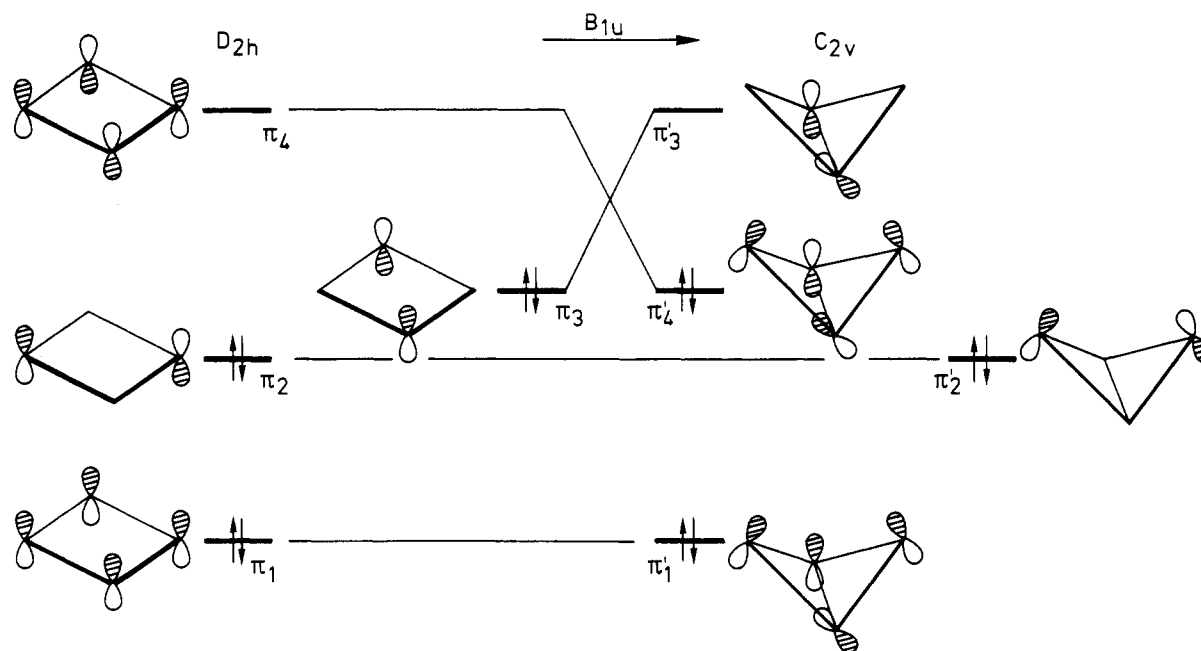


Figure 4. π molecular orbital scheme of 1,3- $X_2Z_2Y_2Z'_2$ rings in D_{2h} and C_{2v} symmetry.

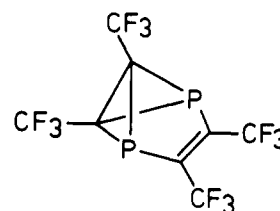
(Table I). The energy differences among these structures possessing a trans-annular PP bridgehead bond are less than 10 kcal/mol with the endo/endo being most stable. The geometric parameters reported in an X-ray analysis of the $[(\eta^5\text{-Cp}^*)_2\text{Zr}(t\text{-BuCP})_2]$ complex¹⁶ possessing two exo *tert*-butyl substituents in a 1,3-diphosphabicyclobutane-2,4-diyl ring with a $C_{2v}(2)$ conformation (PC = 1.897 Å, PP = 2.147 Å, $\theta_1 = 110^\circ$) are in satisfactory agreement with the theoretical 6-31G* data on 3 (PC = 1.927 Å, PP = 2.090 Å, $\theta_1 = 107.6^\circ$). The CC bridgehead bonded $C_{2v}(4)$ conformation 6, however, is lower in energy than 3–5 and only 3.8 kcal/mol above the global C_{2h} minimum 2. It is possible that complexation with Zr in the complex influences the relative energetics of 3 and 6.

The D_{2h} configuration of $P_2H_2C_2^{2-}$ (7) lies significantly higher in energy than its tautomer 1 (Table I). This structure is characterized by an extremely strong negative PP bond order (−0.8 at 6-31G*) and hence the B_{2g} vibrational mode possesses a large imaginary frequency. At the 6-31G* level a second imaginary frequency is found corresponding to a B_{1u} pucker mode. Further optimization at the 6-31G* level within $C_s(1)$ constraint results in a true minimum 8, which is still 110 kcal/mol higher than 2. Structure 8 possesses an almost planar ring with one H substituent strongly out of plane. A 3-21G calculation for 7 (D_{2h}) reveals three imaginary frequencies. The third imaginary frequency is preserved during optimization within $C_s(1)$ constraint leading to 8. Since this points to a ring opening, no further calculations were performed. The CC bridgehead bonded puckered structures 9–11 are energetically clearly preferred over the PP-bridgehead bonded molecule 12. Configurations 9–11 are characterized by a remarkably short CC bond (1.32–1.33 Å) and long PC bonds (2.10–2.12 Å using the 6-31G* basis set). At the 6-31G* level, only the exo/exo conformation 9 corresponds to a true minimum. All other configurations possess one or more imaginary vibrational frequencies. At the 3-21G level no stable minimum for a cyclic $P_2H_2C_2^{2-}$ could be established.

By adding two protons to either 1 or 7 neutral $P_2H_2C_2H_2$ 13, is obtained. The 3-21G optimized D_{2h} geometry displays two imaginary frequencies corresponding to B_{2g} and B_{1u} modes. The out-of-plane vibrations involve the PH bonds and not the CH bonds, as a result of the dominant PP repulsive interaction. Reoptimization of the resulting $C_s(1)$ structure 14, results in a local minimum on the 3-21G potential energy surface. The 6-31G* basis set generally destabilizes the out-of-plane vibrations in substituted 6 π -electron four-membered rings.⁴ Accordingly, the vibration analysis of a 6-31G* optimized D_{2h} structure 13

reveals an additional B_{3g} out-of-plane vibration of the CH bonds. This imaginary vibrational mode is preserved for the $C_s(1)$ stationary point 14 at the 6-31G* level. As a result a barrierless dissociation of the ring is found in a 6-31G* calculation.

Besides the D_{2h} (13) and $C_s(1)$ (14) structures six bicyclobutane-like configurations were considered either with a trans-annular CC (15–17) or PP (18–20) bond. The CC bridgehead bonded isomers are considerably lower in energy and all three conformers correspond to true minima. The endo/endo orientation 16 represents the lowest-energy geometry, only slightly below the endo/exo (17, +0.1 kcal/mol) and exo/exo (15, +2.0 kcal/mol) orientations. There is only one report describing the synthesis of analogues of 15–17 derived from reaction with 1,3,4,6-tetrakis-(trifluoromethyl)-2,5-diphosphatricyclo[3.1.0.0^{2,6}]hex-3-ene:¹⁷



1.2. Nitrogen–Phosphorus Rings (21–41). The unsubstituted 1,3,2,4-diazadiphosphete dianion ($P_2N_2^{2-}$) possesses a stable D_{2h} geometry (21) at all theoretical levels employed in this study. The negative charge is predominantly localized at the nitrogen atoms. Compared to the all-nitrogen analogue (cyclotetrazene, dianion, N_4^{2-}) studied previously,⁴ the harmonic frequency of the B_{1u} pucker mode is significantly reduced. This indicates a more flexible ring. In both basis sets the highest molecular orbitals possess positive eigenvalues, indicating unbound electrons. Neither the $P_2N_2^{2-}$ nor the P_2N_2 molecule has been detected experimentally. The structure of the neutral 1,3,2,4-diazadiphosphete (P_2N_2) has been studied theoretically by Schnöckel et al.¹⁸ Using SCF theory and a DZP quality basis set the most stable isomer of P_2N_2 is a D_{2h} structure (PN = 1.650 Å; NPN = 95.1°), very similar to the present results on the dianion (Table III). Despite the fact that P_2N_2 possesses 4 π electrons, the D_{2h} structure resists bond length alternation and ring opening, parallel to the corresponding dianion 21. Regarding the NN and PP bridgehead bonded puckered configurations of $P_2N_2^{2-}$ the calculations show that the optimized $C_{2v}(4)$ geometries 22 and 23

TABLE I: Total Energies (au) of Four-Membered Rings

X	Y	charge	compd	sym	energy ^{a,b}		X	Y	charge	compd	sym	energy ^{a,b}	
CH	P	-2	1	D _{2h}	-758.024 86 (1)					65	C _{2v} (2)	-1364.443 86 (0)	
					-758.575 74 (1)	c				66	C _{2v} (3)	-1364.454 27 (0)	*
			2	C _{2h}	-758.027 22 (0)	*				67	C _s (2)	-1364.449 71 (0)	
			3	C _{2v} (2)	-757.947 94 (0)		S	C	-2	68	D _{2h}	-870.322 02 (0)	
			4	C _{2v} (3)	-757.963 45 (0)							-870.899 38 (0)	c
			5	C _s (2)	-757.957 77 (0)					71	C _{2v} (4)	-870.453 87 (1)	*
P	CH	-2	6	C _{2v} (4)	-758.021 10 (0)		C	S	-2	72	C _{2v} (4)	-870.131 07 (2)	
PH	C	-2	7	D _{2h}	-757.793 30 (2)		CH	S	0	73	D _{2h}	-871.796 32 (1)	
			8	C _s (1)	-757.852 41 (0)							-872.375 50 (1)	c
			9	C _{2v} (2)	-757.987 53 (0)	*				74	C _{2h}	-871.796 88 (0)	
			10	C _{2v} (3)	-757.983 25 (2)							-872.378 74 (0)	c*
			11	C _s (2)	-757.986 48 (1)					75	C _{2v} (2)	-871.632 49 (0)	
C	PH	-2	12	C _{2v} (4)	-757.777 64 (2)					76	C _{2v} (3)	-871.639 36 (0)	
PH	CH	0	13	D _{2h}	-759.273 34 (3)					77	C _s (2)	-871.640 26 (0)	
			14	C _s (1)	-759.336 46 (1)		S	CH	0	78	C _{2v} (4)	-871.820 52 (0)	*
			15	C _{2v} (2)	-759.411 04 (0)							-872.361 34 (0)	c
			16	C _{2v} (3)	-759.417 65 (0)	*	SH	C	0	79	D _{2h}	-871.230 81 (3)	
			17	C _s (2)	-759.416 18 (0)					80	C _s (1)	-871.778 20 (0)	*
CH	PH	0	18	C _{2v} (2)	-759.247 13 (1)					81	C _{2v} (2)	-871.694 83 (1)	
			19	C _{2v} (3)	-759.249 32 (0)					82	C _{2v} (3)	-871.683 46 (2)	
			20	C _s (2)	-759.251 09 (1)					83	C _s (2)	-871.690 78 (1)	
P	N	-2	21	D _{2h}	-790.089 81 (0)	*	C	SH	0	84	C _{2v} (4)	-871.347 49 (2)	
					-790.700 20 (0)	c	SH	CH	2	85	D _{2h}	-872.032 17 (3)	
			22	C _{2v} (4)	-789.979 73 (0)					86	C _{2v} (2)	-872.217 71 (0)	*
N	P	-2	23	C _{2v} (4)	-789.983 58 (1)					87	C _{2v} (3)	-872.210 63 (0)	
NH	P	0	24	D _{2h}	-791.461 32 (0)	*				88	C _s (2)	-872.216 31 (0)	
					-792.054 93 (0)	c	CH	SH	2	89	C _{2v} (2)	-871.929 95 (3)	
					-792.074 84 (0)	d				90	C _{2v} (3)	-871.936 19 (3)	
			25	C _{2v} (2)	-791.426 43 (0)					91	C _s (2)	dissociation	
			26	C _{2v} (3)	-791.436 98 (0)		S	N	0	92	D _{2h}	-903.770 99 (0)	*
			27	C _s (2)	-791.443 70 (0)							-904.419 92 (0)	c
P	NH	0	28	C _{2v} (4)	-791.311 81 (0)					93	C _{2v} (4)	-903.711 15 (0)	
PH	N	0	29	D _{2h}	-791.281 91 (2)		N	S		94	C _{2v} (4)	-903.611 22 (1)	
			30	C _{2v} (2)	-791.367 05 (0)		NH	S	2	95	D _{2h}	-904.192 03 (0)	*
			31	C _{2v} (3)	-791.367 57 (0)							-904.829 70 (0)	c
			32	C _s (2)	-791.369 58 (0)	*				96	C _{2v} (2)	-904.072 67 (0)	
N	PH	0	33	C _{2v} (4)	-791.277 97 (1)					97	C _{2v} (3)	-904.071 35 (0)	
PH	NH	2	34	D _{2h}	-791.782 83 (2)					98	C _s (2)	-904.079 10 (0)	
			35	C _s (1)	-791.887 18 (0)	*	S	NH	2	99	C _{2v} (4)	-904.090 41 (0)	
			36	C _{2v} (2)	-791.844 12 (0)		SH	N	2	100	D _{2h}	-903.891 76 (2)	
			37	C _{2v} (3)	-791.848 42 (0)					101	C _s (1)	-903.954 44 (0)	
			38	C _s (2)	-791.847 66 (0)					102	C _{2v} (2)	-904.037 26 (0)	*
NH	PH	2	39	C _{2v} (2)	-791.722 81 (0)					103	C _{2v} (3)	dissociation	
			40	C _{2v} (3)	-791.745 96 (0)					104	C _s (2)	-904.026 62 (0)	
			41	C _s (2)	-791.738 15 (0)		N	SH	2	105	C _{2v} (4)	-903.803 19 (2)	
P	O	0	42	D _{2h}	-831.124 46 (0)	*	S	O	2	106	D _{2h}	-943.678 84 (0)	*
					-831.759 14 (0)	c						-944.376 81 (0)	c
			43	C _{2v} (4)	-830.871 70 (3)					107	C _{2v} (4)	-943.502 33 (0)	
O	P	0	44	C _{2v} (4)	-831.116 22 (0)		O	S	2	108	C _{2v} (4)	-943.611 90 (0)	
OH	P	2	45	D _{2h}	-831.448 77 (1)		S	P	0	109	D _{2h}	-1476.449 65 (0)	
			46	C _{2v} (1)	dissociation							-1476.968 71 (0)	c
			47	C _{2v} (3)	-831.504 34 (0)	*				110	C _{2v} (4)	-1476.470 01 (0)	*
			48	C _s (2)	-831.503 82 (0)		P	S	0	111	C _{2v} (4)	-1476.324 65 (0)	
P	OH	2	49	C _{2v} (3)	-831.504 34 (0)	*	PH	S	2	113	D _{2h}	-1476.768 04 (2)	
			50	D _{2h}	-831.322 77 (2)					113	C _s (1)	-1476.834 11 (0)	*
			51	C _s (1)	-831.473 21 (0)	*				114	C _{2v} (2)	-1476.828 74 (0)	
			52	C _{2v} (2)	-831.340 65 (0)					115	C _{2v} (3)	-1476.818 29 (0)	
			53	C _{2v} (3)	-831.346 27 (0)					116	C _s (2)	-1476.824 93 (0)	
			54	C _s (2)	-831.348 52 (0)		S	PH	2	117	C _{2v} (4)	-1476.793 47 (0)	
O	PH	2	55	C _{2v} (4)	-831.336 13 (1)		SH	P	2	118	D _{2h}	-1476.735 95 (2)	
P	P	-2	56	D _{4h}	-1362.766 15 (0)	*				119	C _{2h}	-1476.752 84 (0)	
					-1363.249 16 (0)	c				121	C _{2v} (3)	-1476.846 67 (0)	
			57	C _{2v} (4)	-1362.725 60 (0)					120	C _{2v} (2)	-1476.857 06 (0)	*
PH	P	0	58	D _{2h}	-1363.948 46 (2)					121	C _{2v} (3)	-1476.846 67 (0)	
			59	C _s (1)	-1363.984 18 (0)					122	C _s (2)	-1476.854 77 (0)	
			60	C _{2v} (2)	-1364.039 68 (0)	*	P	SH	2	123	C _{2v} (4)	-1476.642 43 (2)	
			61	C _{2v} (3)	-1364.034 05 (0)		S	S	2	124	D _{4h}	-1589.159 88 (0)	*
			62	C _s (2)	-1364.038 83 (0)							-1589.727 09 (0)	c
			63	C _{2v} (4)	-1363.939 37 (0)					125	C _{2v} (4)	-1589.110 31 (0)	
PH	PH	2	64	D _{4h}	-1364.326 21 (3)								

^a Number of imaginary frequencies in parentheses. ^b Asterisks indicate lowest energy conformer. ^c MP2/6-31G*. ^d MP2/6-31G**.

are significantly higher in energy than D_{2h} structure 21. Only the NN bridgehead bonded isomer corresponds to a true minimum.

Incorporation of two protons as substituents on nitrogen results in a neutral N₂H₂P₂ molecule. Optimization of D_{2h} conformation, 24, produces a local minimum at the 3-21G and 6-31G* levels.

The optimized structure is characterized by an obtuse PNP angle of approximately 101° as a consequence of minimizing the P-P 1,3-repulsive interaction. A Mulliken population analysis indicates considerable electron localization in the ring; nitrogen bears an effective charge of approximately 1 au. These results remain

TABLE II: Harmonic Frequencies (cm⁻¹) of D_{4h} and D_{2h} Structures

X	Y	compd	E_g		B_{2u}	E_u		
			B_{2g}	B_{3g}	B_{1u}	B_{2u}	B_{3u}	
CH	P	1	460i		379	651	804	
			593i		254	717	762	<i>a</i>
PH	C	7	1097i		524i	610	439	
PH	CH	13	1039i	243i	583i	765	687	
P	N	21			502	872	518	
					429	733	674	<i>a</i>
NH	P	24	393		450	566	851	
			94		383	835	776	<i>a</i>
			162		385	834	776	<i>b</i>
PH	N	29	1189i		716i	782	603	
PH	NH	34	1123i	545	751i	696	729	
P	O	42			500	849	37	
					434	728	950	<i>a</i>
OH	P	45	537		373	439i	660	
PH	O	50	1273i		879i	681	513	
P	P	56			251	465	465	
					215	468	468	<i>a</i>
PH	P	58	779i		289i	510	463	
PH	PH	64	802i	802i	557i	559	559	
S	C	68			428	661	487	
					394	828	502	<i>a</i>
CH	S	73	307i		442	748	923	
			497i		330	811	887	<i>a</i>
SH	C	79	71		1521i	6618i	716i	
SH	CH	85	834i	266i	545i	736	718	
S	N	92			535	945	679	
					452	795	755	<i>a</i>
NH	S	95	544		485	694	956	
			361		409	893	841	<i>a</i>
SH	N	100	935i		607i	638	641	
S	O	106			517	903	301	
					424	691	1127	<i>a</i>
S	P	109			255	538	469	
					224	491	595	<i>a</i>
PH	S	112	643i		491i	575	539	
SH	P	118	590i		230i	141	424	
S	S	124			247	571	571	
					212	557	557	<i>a</i>

^a MP2/6-31G*. ^b MP2/6-31G**.

essentially unaffected at the MP2/6-31G* level, although a very low-frequency (94 cm⁻¹) B_{2g} out-of-plane vibration is found and the potential energy surface is very flat. Analogous to the $P_2N_2^{2-}$ dianion, all puckered structures of $N_2H_2P_2$ (25–28) are higher in energy than its planar conformation. The energy ordering among the three conformers with a PP bridgehead bond is 25 > 26 > 27 with a small preference for the endo/exo conformer (27) over the endo/endo structure (26). The configuration with a NN bridgehead bond lies significantly higher in energy. Vibrational analysis shows that all $N_2H_2P_2$ geometries correspond to local minima on the potential energy surface. In contrast with the carbon series, it appears that in the nitrogen series the puckered structures with a PP bridgehead bond are energetically preferred.

The D_{2h} -optimized tautomer $P_2H_2N_2$ (29) with the two protons on phosphorus instead of on nitrogen is significantly higher in energy. Both 3-21G and 6-31G* calculations reveal two large imaginary frequencies for 29. Relaxing the symmetry from D_{2h} to C_s , following the imaginary B_{2g} and B_{1u} vibrations, directly produces a stable strongly puckered bicyclobutane-like minimum 32 ($C_s(2)$). No stationary point corresponding to a $C_s(1)$ type geometry exists. Since both protons are essentially perpendicular to the NPN planes there is no allylic fragment in this structure. The NPN angles are very small (53–54°) and the trans-annular NN distance (1.560 Å using 6-31G*) is considerably less than in the D_{2h} structure. Surprisingly the corresponding NN bond order of -0.06 still indicates a small repulsive interaction. Besides 32 (endo/exo), also the 30 (exo/exo) and 31 (endo/endo) conformations represent stable minima or the potential energy surface. Energy differences among these structures are small (<2 kcal/mol) although 32 is slightly preferred. For $P_2H_2N_2$ the

TABLE III: Geometry of D_{2h} and D_{4h} Conformations^a

X	Y	compd	XY	$\angle YXY$	XH	YH
CH	P	1	1.772	96.2	1.082	
			1.791	97.2	1.087	
PH	C	7	1.778	103.6	1.413	<i>b</i>
PH	CH	13	1.720	92.3	1.376	1.065
P	N	21	1.682	89.2		
			1.733	92.0		<i>b</i>
NH	P	24	1.689	100.2	0.996	
			1.721	101.1	1.015	<i>b</i>
			1.720	101.3	1.008	<i>c</i>
PH	N	29	1.633	95.8	1.370	
PH	NH	34	1.647	85.4	1.391	1.013
P	O	42	1.637	82.6		
			1.692	83.4		<i>b</i>
OH	P	45	1.750	107.0	0.981	
PH	O	50	1.598	85.7	1.407	
P	P	56	2.146	90.0		<i>b</i>
			2.168	90.0		
PH	P	58	2.097	103.0	1.381	
PH	PH	64	2.057	90.0	1.389	1.389
S	C	68	1.766	94.3		<i>b</i>
			1.823	95.5		<i>b</i>
CH	S	73	1.687	96.2	1.066	
			1.711	96.8	1.071	<i>b</i>
SH	C	79	1.696	74.3	1.661	
SH	CH	85	1.681	88.4	1.350	1.075
S	N	92	1.614	89.3		<i>b</i>
			1.684	90.7		<i>d</i>
			1.654	89.6		
NH	S	95	1.625	99.9	1.022	
			1.673	100.4	1.042	<i>b</i>
SH	N	100	1.610	94.4	1.371	
S	O	106	1.588	81.6		<i>b</i>
			1.681	83.0		<i>b</i>
S	P	109	2.061	92.3		<i>b</i>
			2.097	92.4		
PH	S	112	2.016	97.3	1.393	
SH	P	118	2.121	104.7	1.344	
S	S	124	1.990	90.0		<i>b</i>
			2.065	90.0		<i>d</i>
			2.0	90.0		

^a Distances in Å, angles in degrees. ^b MP2/6-31G*. ^c MP2/6-31G**. ^d Experimental values.

NN bridgehead bond configurations are lower in energy than the isomer with a trans-annular PP bond (33). The latter does not correspond to a stable minimum on the potential energy surface. Despite of a considerable gain in energy with respect to the planar conformation 29, the puckered structures 30–32 remain higher in energy than the planar tautomer 24.

It is well-established that neutral 1,2,3,4-diazadiphosphetides (8 π electrons) can adopt both a cis and a trans orientation of the substituents on phosphorus.¹⁹ No experimental data are available on 6 π electron dication derivatives. For the 6 π dication ($P_2H_2N_2H_2^{2+}$) where all ring nuclei carry a hydrogen substituent, a low-frequency out-of-plane vibration of the PH bonds can be anticipated. This is confirmed, at the 3-21G and 6-31G* levels by the imaginary frequency of the gerade B_{2g} and the ungerade B_{1u} out-of-plane PH vibrations of the D_{2h} -optimized geometry (34). When the symmetry is lowered accordingly to C_s , further optimization results in a stable arrangement 35 ($C_s(1)$) containing an essentially planar phosphorus-centred allylic fragment ($PHN_2H_2^+$) loosely bound to a PH^+ moiety. Apparently protonation of the nitrogen nuclei suppresses the direct formation of a trans-annular NN bridgehead bond as in 32. Nevertheless, several bicyclobutane-like minima exist for the $P_2H_2N_2H_2^{2+}$ dication although they are all higher in energy than the $C_s(1)$ structure (35). At the 6-31G* level six different isomers (36–41) are found, three with a NN and three with a PP bridgehead bond. There is a clear preference for the NN bridgehead bond for which the endo/endo orientation of the hydrogens (37) is lowest in energy. At the 3-21G level geometry optimization of the three PP bridgehead bonded conformations invariably results in a single structure with an endo/endo orientation.

TABLE IV: Geometry of C_{2h} , C_s , and C_2 Conformations^a

X	Y	compd	sym	X ₁ Y	X ₂ Y	YY	∠YX ₁ Y	θ ₁ ^b	θ ₂ ^b	θ ₃ ^b
CH	P	2	C_{2h}	1.781	1.781	2.643	95.8	180.0	154.9	205.1
		3	$C_{2v}(2)$	1.927	1.927	2.090	65.7	107.6	106.6	106.6
		4	$C_{2v}(3)$	1.907	1.907	2.087	66.4	120.9	253.2	253.2
		5	$C_s(2)$	1.900	1.930	2.088	66.6	113.1	105.5	250.6
P PH	CH C	6	$C_{2v}(4)$	1.876	1.876	1.479	46.4	127.7		
		8	$C_s(1)$	1.701	1.886	2.807	111.2	177.4	200.9	116.3
		9	$C_{2v}(2)$	2.104	2.104	1.327	36.8	104.5	94.9	94.9
		10	$C_{2v}(3)$	2.118	2.118	1.320	33.7	114.6	262.8	262.8
C PH	PH CH	11	$C_s(2)$	2.107	2.104	1.325	36.7	108.4	99.8	264.6
		12	$C_{2v}(4)$	1.851	1.851	2.052	67.3	143.7		
		14	$C_s(1)$	1.647	1.834	2.882	97.8	176.1	193.1	106.7
		15	$C_{2v}(2)$	1.833	1.833	1.469	47.3	114.8	96.6	96.6
CH	PH	16	$C_{2v}(3)$	1.810	1.810	1.514	49.5	126.8	257.2	257.2
		17	$C_s(2)$	1.814	1.824	1.491	48.5	119.5	257.5	97.7
		18	$C_{2v}(2)$	1.814	1.814	2.178	73.8	130.1	124.8	124.8
		19	$C_{2v}(3)$	1.844	1.844	2.154	71.5	151.1	247.8	247.8
P N NH	N P P	20	$C_s(2)$	1.825	1.824	2.167	72.9	139.2	247.2	129.0
		22	$C_{2v}(4)$	1.813	1.813	1.451	47.2	116.0		
		23	$C_{2v}(4)$	1.771	1.771	1.985	68.1	117.1		
		25	$C_{2v}(2)$	1.777	1.777	2.054	70.6	104.0	117.5	117.5
P PH	NH N	26	$C_{2v}(3)$	1.767	1.767	2.045	70.7	116.0	237.6	237.6
		27	$C_s(2)$	1.754	1.791	2.048	71.4	108.3	118.4	239.2
		28	$C_{2v}(4)$	1.841	1.841	1.455	46.5	130.5		
		30	$C_{2v}(2)$	1.740	1.740	1.517	51.7	111.8	98.2	98.2
N PH	PH NH	31	$C_{2v}(3)$	1.717	1.717	1.606	55.8	127.5	257.0	257.0
		32	$C_s(2)$	1.723	1.730	1.560	53.8	118.2	257.3	99.3
		33	$C_{2v}(4)$	1.694	1.694	2.077	75.6	140.1		
		35	$C_s(1)$	1.553	1.860	2.286	94.7	175.0	184.0	96.7
NH	PH	36	$C_{2v}(2)$	1.831	1.831	1.448	46.6	120.1	93.4	93.4
		37	$C_{2v}(3)$	1.821	1.821	1.471	47.6	133.9	264.6	264.6
		38	$C_s(2)$	1.820	1.831	1.458	47.2	126.1	265.0	94.3
		39	$C_{2v}(2)$	1.736	1.736	1.965	68.9	108.7	127.4	127.4
P O OH	O P P	40	$C_{2v}(3)$	1.724	1.724	1.941	68.5	124.6	223.7	223.7
		41	$C_s(2)$	1.710	1.752	1.951	69.6	115.3	228.6	131.8
		43	$C_{2v}(4)$	1.921	1.921	1.459	44.6	68.5		
		44	$C_{2v}(4)$	1.698	1.698	1.997	72.1	111.2		
P PH	OH O	47	$C_{2v}(2)$	1.780	1.780	2.104	72.5	108.6	210.5	210.5
		48	$C_s(2)$	1.767	1.807	2.104	73.1	101.6	218.5	138.4
		49	$C_{2v}(2)$	1.780	1.780	2.330	81.8	102.9		
		51	$C_s(1)$	1.485	1.902	2.282	100.4	175.7	181.6	93.2
O P PH	PH P P	52	$C_{2v}(2)$	1.819	1.819	1.476	47.9	132.1	91.4	91.4
		53	$C_{2v}(3)$	1.811	1.811	1.493	48.7	147.9	265.9	265.9
		54	$C_s(2)$	1.809	1.819	1.485	48.5	139.4	265.6	91.9
		55	$C_{2v}(4)$	1.659	1.659	1.928	71.1	116.3		
P PH	PH P P	57	$C_{2v}(4)$	2.244	2.244	2.132	56.7	114.0		
		59	$C_s(1)$	2.043	2.676	3.294	107.4	173.7	196.2	110.5
		60	$C_{2v}(2)$	2.212	2.212	2.162	58.5	98.4	97.4	97.4
		61	$C_{2v}(3)$	2.204	2.204	2.193	59.7	112.8	257.4	257.4
P PH	PH PH PH	62	$C_s(2)$	2.203	2.209	2.178	59.2	104.5	258.0	98.9
		63	$C_{2v}(4)$	2.184	2.184	2.212	60.9	137.2		
		65	$C_{2v}(2)$	2.224	2.224	2.326	63.1	126.8	97.4	97.4
		66	$C_{2v}(3)$	2.216	2.216	2.311	62.8	143.3	266.2	266.2
S C CH	C S D	67	$C_s(2)$	2.230	2.208	2.319	62.7	135.2	98.3	240.3
		71	$C_{2v}(4)$	2.070	2.070	1.335	37.6	112.6		
		72	$C_{2v}(4)$	2.235	2.235	2.040	54.3	123.9		
		74	C_{2h}	1.691	1.691	2.513	96.0	180.0	161.5	198.5
S	CH		C_{2h}^c	1.721	1.721	2.570	96.6	180.8	166.4	193.6
		75	$C_{2v}(2)$	1.903	1.903	1.991	63.1	104.4	104.4	104.4
		76	$C_{2v}(3)$	1.875	1.875	1.976	63.6	121.6	254.1	254.1
		77	$C_s(2)$	1.879	1.895	1.983	63.7	110.9	256.7	108.2
SH	C	78	$C_{2v}(4)$	1.794	1.794	1.419	46.6	117.9		
			$C_{2v}(4)^c$	1.807	1.807	1.429	46.6	118.9		
		80	$C_s(1)$	1.775	2.624	3.181	127.3	176.1		
		81	$C_{2v}(2)$	2.012	2.012	1.350	39.2	100.5	94.7	94.7
C SH	SH CH	82	$C_{2v}(3)$	2.019	2.010	1.347	39.0	111.9	258.1	258.1
		83	$C_s(2)$	2.014	2.013	1.347	39.1	104.7	101.2	264.5
		84	$C_{2v}(4)$	2.726	2.726	2.102	45.4	147.4		
		86	$C_{2v}(2)$	1.826	1.826	1.406	45.3	108.1	96.8	96.8
CH	SH	87	$C_{2v}(3)$	1.800	1.800	1.435	47.0	121.6	254.5	254.5
		88	$C_s(2)$	1.807	1.818	1.418	46.2	113.8	262.0	98.0
		89	$C_{2v}(2)$	2.392	2.392	2.118	52.5	125.2	99.6	99.6
		90	$C_{2v}(3)$	2.363	2.363	2.106	52.9	168.8	262.8	262.8
S N NH	N S S	93	$C_{2v}(4)$	1.760	1.760	1.372	45.8	111.5		
		94	$C_{2v}(4)$	1.736	1.736	1.896	66.6	114.6		
		96	$C_{2v}(2)$	1.736	1.736	1.977	69.4	101.9	120.9	120.9
		97	$C_{2v}(3)$	1.714	1.714	1.961	69.8	117.8	127.6	127.6
S	NH	98	$C_s(2)$	1.705	1.747	1.968	70.5	108.3	237.8	124.3
		99	$C_{2v}(4)$	1.762	1.762	1.415	52.1	123.1		

TABLE IV: (Continued)

X	Y	compd	sym	X ₁ Y	X ₂ Y	YY	$\angle YX_1Y$	θ_1^b	θ_2^b	
SH	N	101	C _s (1)	1.528	1.745	2.375	102.0	175.1	187.1	104.1
		102	C _{2v} (2)	1.802	1.802	1.317	42.9	107.2	94.4	94.4
		104	C _s (2)	1.808	1.821	1.300	42.1	113.0	100.3	265.4
N	SH	105	C _{2v} (4)	1.769	1.769	2.037	70.3	134.8		
S	O	107	C _{2v} (4)	1.775	1.775	1.452	48.3	125.2		
O	S	108	C _{2v} (4)	1.661	1.661	1.932	71.1	109.2		
S	P	110	C _{2v} (4)	2.136	2.136	2.097	58.8	108.6		
P	S	111	C _{2v} (4)	2.209	2.209	2.026	54.6	114.5		
PH	S	113	C _s (1)	1.943	2.243	3.113	106.5	171.7	180.7	97.8
		114	C _{2v} (2)	2.199	2.199	2.062	55.9	101.9	94.0	94.0
		115	C _{2v} (3)	2.199	2.199	2.077	56.4	118.4	262.9	262.9
		116	C _s (2)	2.196	2.197	2.070	56.2	109.3	264.5	95.3
S	PH	117	C _{2v} (4)	2.084	2.084	2.296	66.9	131.0		
SH	P	119	C _{2h}	2.132	2.132	3.327	102.5	180.0	222.9	137.1
		120	C _{2v} (2)	2.199	2.199	2.152	58.6	95.6	100.5	100.5
		121	C _{2v} (3)	2.191	2.191	2.180	59.7	110.5	250.9	250.9
		122	C _s (2)	2.185	2.202	2.167	59.4	101.8	254.4	102.6
P	SH	123	C _{2v} (4)	2.476	2.476	2.108	50.4	138.7		
S	S	125	C _{2v} (4)	2.091	2.091	1.014	57.6	109.5		

^a Distances in Å, angles in degrees. ^b θ_1 , θ_2 , and θ_3 defined in Figure 2. ^c MP2 calculation.

1.3. Oxygen-Phosphorus Rings (42–55). The P₂O₂ molecule has been subject of recent experimental and theoretical studies^{20–23} Peyerimhoff et al.²¹ report that at the SCF/6-31G* level the cyclic D_{2h} structure is more stable than open-chain conformations, in agreement with earlier semi-empirical MNDO calculations by Baird.²³ Peyerimhoff et al. calculated the optimized D_{2h} geometry of cyclic P₂O₂ at various theoretical levels, starting with SCF/6-31G* up to MRD-CI/DZP. As a result they find a small but significant elongation of the PO bond upon inclusion of electron correlation from 1.637 Å using SCF/6-31G* to 1.671 Å at the MRD-CI/DZP level. At the three theoretical levels employed in the present study (of which the 6-31G* calculation is identical to that in ref 21) the D_{2h} conformation **42** corresponds to a stable minimum. It is important to note that the inclusion of MP2 theory has a strong effect on the harmonic vibrational frequency of the planar B_{3u} ring deformation which changes from 37 to 950 cm⁻¹. With respect to experimental evidence concerning the formation of a cyclic D_{2h} P₂O₂ conformation no conclusive answer can be given. In a study on matrix reaction of P₂ and O₃ Mielke et al.²⁰ tentatively assign a sharp infrared band at 1155 cm⁻¹ to an open-chain trans-OPPO structure. This assignment is based on a close agreement with the antisymmetric PO fundamental of 1150 cm⁻¹ obtained by Lohr from ab initio calculations on this structure.²² However, Lohr did not consider the possibility of a cyclic D_{2h} P₂O₂ conformation and, mistakenly, arrives at the conclusion that the trans-OPPO structure is the global minimum for P₂O₂. The two puckered C_{2v}(4) structures of P₂O₂ are both higher in energy than the D_{2h} configuration. The C_{2v}(4) OO bridgehead bonded structure **43** lies 158 kcal/mol above **42** at the 6-31G* level and possesses three imaginary vibrational frequencies. The isomer with the PP bridgehead bond corresponds to a stable minimum and is only slightly above the planar minimum (+5.2 kcal/mol).

Protonation of the two oxygen nuclei gives the O₂H₂P₂²⁺ molecule. At the 3-21G level, the D_{2h} geometry, **42**, corresponds to a stable minimum. However, using the 6-31G* basis set an imaginary frequency for the planar B_{2u} ring deformation is calculated. The positive charge is predominantly localized on phosphorus. Both stationary points are characterized by a rhomboidal structure with an obtuse POP angle of approximately 107°. When the symmetry is lowered from D_{2h} to C_{2v} (**43**) a barrierless dissociation of O₂H₂P₂²⁺ molecule is found at the 6-31G* level, resulting in an allylic OHP₂⁺ fragment and a OH⁺ moiety. With respect to the puckered structures, the O₂H₂P₂²⁺ isomer shows a somewhat anomalous behaviour. At the 3-21G level all optimizations starting from initial C_{2v}(2), C_{2v}(3), C_s(2), and C_{2v}(4) type of structures give rise to a single minimum with a bridgehead PP bond and an exo/exo orientation of the hydrogen nuclei (C_{2v}(2), **47**). Most remarkable is the fact that even

geometries with an initial OO trans-annular bond rearrange without any energy barrier to the PP bonded isomers. In Tables I and IV structures **47** and **49** are therefore identical. At the 6-31G* level the behavior is completely identical with the exception that in addition a stable endo/exo conformer (**48**, C_s(2)) is found only 0.3 kcal/mol above **47/49**. Structure **47/49** represents the lowest energy configuration for a 1,3-cyclic O₂H₂P₂²⁺ molecule.

The alternative D_{2h} configuration with two protons on phosphorus (P₂H₂O₂²⁺, **50**), the dication of 1,3,2,4-dioxadiphosphetane,²⁴ possesses two imaginary vibrational frequencies both at the 3-21G and 6-31G* levels. Again the positive charge is localized on the P nuclei. The combined effect of the gerade and ungerade (B_{2g} and B_{1u}) out-of-plane vibrations lead to a structure of C_s(1) symmetry (**51**), which corresponds to a local minimum. This C_s(1) configuration possesses two short (1.485 Å) and two long (1.902 Å) bonds and consists of a PHO₂⁺ allylic fragment and a PH⁺ moiety. Except for the hydrogen nucleus of the PH⁺ group, which is strongly out of plane, the ring is almost planar. The bicyclobutane-like geometries of P₂H₂O₂²⁺ with a OO bridgehead bond (**52–54**) are local minima on the potential energy surface, but are significantly higher in energy than **51**. The calculated energy difference of **51** and **52–54** amounts to 78–83 kcal/mol at the 6-31G* level. The optimized PP bridgehead bonded bicyclobutane-like configuration **55** (C_{2v}(4)) possesses one imaginary vibrational frequency and is energetically least favored. Finally, it is to be noted that the P₂H₂O₂²⁺ isomers are continuously higher in energy than their O₂H₂P₂²⁺ tautomers.

1.4. Phosphorus Rings (56–66). Scherer and co-workers first succeeded in stabilizing a nearly square P₄ ring as a ligand in a [Cp*(CO)₂Nb(P₄)] complex.²⁵ The four P atoms form a planar slightly distorted square with a mean PP side of 2.159 Å. Very recently Sheer et al. reported the synthesis and X-ray structure of [Cp*Rh(η⁴-[PCr(CO)₃]₄)], with Cp' = C₅H₄-*t*-Bu, incorporating a similar P₄ ring with bond PP lengths ranging from 2.143 to 2.160 Å (average 2.149 Å).²⁶ Other complexes with a rectangular planar P₄ unit are known, like the [Cp*Rh(P₄)RhCp*] triple decker containing P₄ with a short side of 2.052 Å and a long side of 2.845 Å. These geometric differences among P₄ rings probably reflect the valence electron distribution in the complexes with either a square 6e donor (P₄²⁻) or a rectangular 4e donor (P₄). On the other hand, ab initio calculations on planar, neutral 4 π -electron P₄ molecules have shown that in contrast with first-row analogues the P₄ square does not possess any tendency to undergo distortion to rectangular structures.²⁷ The present study reveals that the tetraphosphete dianion (P₄²⁻, **56**) is a stable structure within D_{4h} symmetry at all levels of theory. The PP distance of 2.168 Å (MP2/6-31G*) is in excellent agreement with the X-ray data on [Cp*(CO)₂Nb(P₄)] and [Cp*Rh(η⁴-[PCr-

(CO)₅][4]. The harmonic frequency of the B_{1u} pucker mode is rather small (215 cm⁻¹ for a MP2/6-31G* calculation) and indicates a flexible ring. The highest occupied molecular orbitals possess a positive eigenvalue. The puckered C_{2v}(4) isomer of P₄²⁻ 57 also corresponds to a true minimum although it is 20–25 kcal/mol higher in energy than the planar conformation 56. The geometry of 57 is in good agreement with the X-ray crystallographic analysis on the [Cp*(CO)CoP₄] complex, formed as an oxidative addition product in the reaction of white phosphorus (P₄) and [Cp*Co(μ-CO)]₂.²⁸ The P₄²⁻ ligand in this complex possesses a formal charge of -2 au and its geometry is based on the tetrahedral structure of P₄ in which one edge is opened and bridged by the Cp*Co(CO) moiety. Characteristic geometric data are PP(edge) = 2.210 Å; PP(bridge) = 2.158 Å; and folding angle θ₁ = 95.0° compared to 2.244 Å; 2.132 Å; and 114.0° for the same parameters of isolated C_{2v}(4) P₄²⁻ (57) at the 6-31G* level. In their recent study Sheer et al.²⁶ report a similar structure for a puckered P₄ unit in [Cp'(CO)Rh{η²-[PCr(CO)₃]₄}] (PP(edge) = 2.222 Å; PP(bridge) = 2.201 Å; θ₁ = 94°). The elongation of the PP bonds has been ascribed to steric interaction of the bulky Cr(CO)₃ fragments. Baudler and co-workers describe the synthesis of metal salts of the tetraphosphabicyclo[1.1.0]butane conjugate acid (M⁺P₄H⁻, M = Li, Na, K).²⁹ Its structure can be regarded as a mono protonated (endo) P₄²⁻ ion.

The P₄H₂ molecule has been identified using mass spectroscopy in mixtures of phosphines³⁰ but has never been isolated as a pure compound. The molecule is expected to possess a bicyclobutane-like geometry. Ab initio calculations by Schoeller et al. indeed show that the D_{2h} geometry is not the lowest-energy conformation of P₄H₂.³¹ Using SCF/STO-3G calculations they find that the D_{2h} structure lies 163 kcal/mol above the tetraphosphabicyclobutane minimum. The energy differences among the three structural conformers of the tetraphosphabicyclobutane structure (exo/exo; exo/endo; endo/endo) are relatively small at the MNDO level, the C_{2v} exo/exo conformation being the absolute minimum. In a second study Schoeller et al.³² investigated the electronic structure of these C_{2v} tetraphosphabicyclobutane derivatives in more detail at their fixed experimental geometries^{33,34} using various basis sets, optionally including electron correlation via PNO-CI and CEPA. In the present study full geometry optimizations were performed at the 3-21G and 6-31G* SCF levels within D_{2h}, C_s, and C_{2v} symmetry constraints. The D_{2h} stationary point (58) possesses two imaginary frequencies for the B_{2g} and B_{1u} modes respectively. After subsequent relaxation of the resulting C_s(1) structure a stable minimum (59) is obtained. The C_s(1) conformer consists of allylic PPHP and PH fragments. In addition two C_{2v} conformations (exo/exo, 60, C_{2v}(2)) and (endo/endo, 61, C_{2v}(3)) as well as a C_s(2) structure 59 were investigated. In agreement with the MNDO calculations of Schoeller the exo/exo conformation (60) is preferred. The geometric parameters of 60 at the 6-31G* level are in good agreement with experimental X-ray data on the exo/exo conformers of 1,3-bis(2,4,6-tri-*tert*-butylphenyl)tetraphosphabicyclobutane³³ and 1,3-bis(bis(trimethylsilyl)amino)tetraphosphabicyclobutane.³⁴ Also an endo/endo orientation has been reported in the X-ray crystallographic analysis of the tricyclic P₆(C₅Me₅)₂ molecule.³⁵ In this molecule the endo/endo orientation is anchored by a bridging C₅Me₅-P-P-C₅Me₅ moiety. Finally, the endo/exo isomer of 1,3-bis(2,4,6-tri-*tert*-butylphenyl)phosphabicyclobutane has been identified in solution using ³¹P NMR but was found to be thermally unstable.³⁶ A related triphosphabicyclobutane (ArP(P₂)C(SiMe₃)₂, Ar = 2,4,6-tri-*tert*-butylphenyl) has been reported containing one exo substituent.³⁷ Selected geometric parameters from experimental and theoretical studies are collected in Table V.

For the neutral tetraphosphetane (P₄H₄) molecule (8π electrons) recent ab initio calculations^{38,39} reveal a slightly folded four-membered ring with an all-trans arrangement of the PH bonds as the lowest-energy conformation (D_{2d}). This is very similar to X-ray structures of derivatives with various substit-

TABLE V: Geometric Parameters for C₂, P₂R₂P₂ Molecules

	R	PP' (Å)	PP' (Å)	θ ₁ (deg)	θ ₂ (deg)
MNDO	H	2.045	2.046	102.6	103.7
STO-3G	H	2.176	2.150	100.8	96.5
3-21G	H	2.415	2.396	98.4	94.7
6-31G*	H ^a	2.212	2.162	98.4	97.4
6-31G*	H ^b	2.204	2.193	112.8	257.4
X-ray ^{a,c}	Ar ^d	2.229	2.166	95.5	105.4
X-ray ^{a,e}	(Me ₃ Si) ₂ N	2.217	2.129	95.2	109.9
X-ray ^{b,f}	C ₅ Me ₅ P ⁻	2.187	2.160	115.5	g
X-ray ^{a,h}	Ar ^d	2.227	2.136	105.0	g

^a Exo/exo conformer. ^b Endo/endo conformer. ^c Reference 33. ^d Ar = 2,4,6-tri-*tert*-butylphenyl. ^e Reference 34. ^f Reference 35. ^g Not reported. ^h Reference 37; corresponds to ArP(P₂)C(SiMe₃)₂.

uents.⁴⁰ For the molecule of interest in the present study, the tetraphosphetane dication P₄H₄²⁺ with 6π electrons, available data are scarce. Schäfer et al.⁴¹ have performed an experimental and theoretical MNDO study on the dication. They report that the dication, generated via cyclic voltammetry, is unstable and rapid rearrangements occur at a low temperature of -100 °C. In fact the dication undergoes a rapid 1,2 shift with a subsequent decomposition into a disubstituted phosphonium cation and P₂. MNDO calculations are in line with these results. It is therefore not surprising that the D_{4h} P₄H₄²⁺ dication is not stable at the 3-21G and 6-31G* levels. A total of three imaginary frequencies is found (E_g and B_{2u}) indicating ring opening. Also the puckered isomers of P₄H₄²⁺ (65–67) have been optimized. At the 3-21G level the endo/exo conformation C_s(2) is preferred, whereas at the 6-31G* level the endo/endo C_{2v}(3) conformation is the global minimum of cyclic P₄H₄²⁺ isomers. Optimization at the 3-21G level within a C_{2v}(3) constraint reveals a highly symmetric structure corresponding to a D_{2d} point group. This D_{2d} configuration possesses five imaginary vibrational frequencies and is unstable.

1.5. Carbon-Sulfur Rings (68–91). The S₂C₂²⁻ dianion, is experimentally unknown. At the 3-21G level the optimized D_{2h} configuration of S₂C₂²⁻ (68) possesses a single imaginary frequency for the B_{2u} planar ring deformation mode. Subsequent optimization of the C_{2v}(1) geometry (69) results in a new stationary point which is not a stable minimum but possesses an imaginary-frequency vibrational mode. Relaxation along this direction yields an acyclic stable C_s minimum (70). In contrast with the 3-21G results, SCF and MP2 calculations with a 6-31G* basis set predict the D_{2h} structure to be a stable minimum. Both C_{2v}(4) puckered structures of the S₂C₂²⁻ (71 and 72) possess one or two imaginary vibrational frequencies at their optimized geometries depending on the theoretical level. The puckered configuration with a CC bridgehead bond (71) is energetically preferred and is also lower in energy than the planar D_{2h} structure.

Various derivatives of C₂H₂S₂ have received experimental and theoretical attention.^{42–45} In the most recent study by Hess et al.,⁴² MP2/6-31G* calculations indicate that the *trans*-dithioglyoxal (-872.401 31 au, 0 kcal/mol) is more stable than its valence isomers 1,2-dithiete (+5.5 kcal/mol), and *cis*- or *gauche*-dithioglyoxal (+4.3 and +4.2 kcal/mol). Accompanying IR data, however, unequivocally suggest 1,2-dithiete to be the most stable isomer. The single report which has taken the 1,3-dithiete isomer into account is a study by Haddon et al.⁴⁵ They found that 1,3-dithiete lies 40–70 kcal/mol above the 1,2-dithiete isomer depending on the theoretical level. The present study concentrates on 1,3-dithiete configurations. At the 3-21G level the D_{2h} conformer (73) is a stable minimum. SCF/6-31G* and MP2/6-31G* calculations reveal a single imaginary frequency for the B_{2g} hydrogen out-of-plane vibration. The D_{2h} MP2/6-31G* stationary point is only moderately above (+16.2 kcal/mol) the *trans*-dithioglyoxal minimum reported by Hess et al.⁴² Hence, the energy difference is much less than calculated by Haddon et al.⁴⁵ Geometry optimization of the D_{2h} conformer along the imaginary B_{2g} mode reveals a stable C_{2h} structure (74) with a slightly lower energy (14.2 kcal/mol above *trans*-dithioglyoxal

TABLE VI: Experimental and Theoretical Harmonic Frequency Data (cm⁻¹) for S₂N₂

mode ^a	SCF ^b 7s3p1d	CEPA ^b 10s6p1d	SCF 6-31G*	MP2 6-31G*	WC ^c	BE ^d	ID ^e
A _g	1125	983	1123	836		665	
A _g	760	676	748	602			605, 608
B _{1g}	1080	997	1085	884			
B _{1u}	533	527	535	452	474	476	
B _{2u}	954	898	945	795	791	785	
B _{3u}	632	756	679	755	652		

^a The present irrep notation differs from ref 58 due to a different choice of coordinates, for direct comparison B_{2u} and B_{3u} should be interchanged.

^b Reference 58. ^c Reference 46. ^d Reference 47, additional harmonic frequencies of 90.9 and 221 cm⁻¹ are reported but probably do not correspond to normal modes of the isolated molecule. ^e Reference 48, an additional frequency of 168 cm⁻¹ has been assigned to a lattice mode.⁵⁸

at MP2/6-31G*). With respect to the bicyclobutane-like structures four configurations (75–78) can be envisaged. The calculations show that the optimized geometries with a SS bridgehead bond (75–77) are invariably higher in energy than the planar *D*_{2h} configuration 73. Structures 75–77 are true minima at the 6-31G* level but the endo/endo (*C*_{2v}(3)) and endo/exo (*C*_s(2)) conformers are transition states on the 3-21G potential energy surface. The isomer with the CC bridgehead bond (2,4-dithiabicyclo[1.1.0]butane, 78) is the lowest energy minimum at both the 3-21G and 6-31G* levels for the C₂H₂S₂ structures considered in the present study. An MP2/6-31G* calculation (Tables I and IV) reveals, however, that the effect of electron correlation is less for 78 than for 73 and 74. The MP2/6-31G* calculation establishes that the puckered configuration is less stable than the *D*_{2h} and *C*_{2h} structures, and places 78 25 kcal/mol above *trans*-dithioglyoxal. As a conclusion the present MP2/6-31G* calculations on C₂H₂S₂ confirm the 1,3-dithiete to be the highest energy isomer although the difference with *trans*-dithioglyoxal is modest.

Another isomer places the two protons of the 1,3-substituted ring on the sulfur atoms, leading two S₂H₂C₂. Geometry optimization of the *D*_{2h} conformer (79) at the 3-21G and 6-31G* level reveals a rhomboidal structure with an acute CSC angle of 69.3° and 74.3° respectively. At the 6-31G* level, the energy of 79 lies much above (+272 kcal/mol) the *D*_{2h} tautomer C₂H₂S₂ 73. Despite the fact that 79 possesses a number of very large imaginary frequencies, optimization within *C*_s(1) constraint yields a true minimum (80) with a much lower energy, but still significantly above the isomers 73 and 74. The bicyclobutane-like configurations of S₂H₂C₂ 81–84 are all higher in energy than the *C*_s(1) minimum 80, at both levels and do not correspond to true minima.

The energy-optimized *D*_{2h} conformer of the S₂H₂C₂H₂²⁺ dication 85 possesses two imaginary vibrational frequencies at the 3-21G level for the B_{2g} and B_{1u} pucker modes. An additional imaginary B_{3g} pucker mode is found using a 6-31G* basis. Continuation of the geometry optimization at the 3-21G level according to the imposed energy-lowering vibrations results in a stable *C*_{2v}(2) geometry corresponding to a bicyclobutane-like structure 86 well below (–118 kcal/mol) the original *D*_{2h} configuration 85. This structure is characterized by a short, transannular C–C bond of 1.390 Å. Surprisingly, the calculated C–C bond order is negative (–0.43). Structure 86 also corresponds to a stable minimum at the 6-31G* level. Other bicyclobutane-like configurations exist. In addition to the CC bridgehead bonded isomer 86 (exo/exo) the endo/endo (87) and endo/exo (88) structures correspond to stable minima, lying only slightly above 86 at the 6-31G* level (+4.4 and +0.8 kcal/mol). The alternative configurations with a SS bridgehead bond (89–91) are significantly higher in energy and their stationary points possess several imaginary vibrational frequencies. The *C*_s(2) structure 91 even dissociates within *C*_s symmetry constraint without any energy barrier into CHS₂H₂⁺ and CH⁺ at both levels.

1.6. Nitrogen–Sulfur Rings (92–105). Sulfur–nitrogen rings have been subject of many recent studies and form a large class of aromatic inorganic rings. The cyclic 1,3,2,4-dithiadiazetidine (S₂N₂) molecule has been synthesized^{10a} and is well characterized by several spectroscopic techniques (IR,^{46,47} Raman,⁴⁸ and PES⁴⁹)

and X-ray crystallography.^{50,51} The widespread interest in S₂N₂ is partially a result of the fact that polysulfurnitride, (SN)_x, obtained in a topochemical solid-state polymerization of S₂N₂ is metallic⁵² and represents the first superconducting polymer.⁵³ It is therefore not surprising that a number of theoretical studies at various levels have been concerned with the geometry, the spectral or the electronic properties of the S₂N₂ molecule^{45,54–61} and the (SN)_x polymer.^{62–64}

The most advanced theoretical calculations on S₂N₂ are reported by Palmer and Guest⁵⁵ describing CI/DZP calculations on the lowest singlet and triplet states and the UV spectrum at the experimental geometry. Tang et al.⁶⁰ report SCF/6-21G* geometry optimization for S₂N₂. In an earlier paper Karpfen et al.⁵⁸ describe geometry optimization and vibrational analysis at the PNO-CI and CEPA-PNO levels using large Gaussian basis sets. The S₂N₂ molecule is found to be stable at all levels of theory. The present calculations on S₂N₂ are an extension of our previous study⁴ and include second order Møller–Plesset perturbation theory. Comparing the MP2/6-31G* results with those obtained at other levels, the final energy is the lowest reported so far. With respect to the experimental SN distance (1.654 Å) in the solid state, the MP2/6-31G* calculations slightly overestimate the ring size (1.684 Å). The calculated harmonic vibrational frequencies show considerable scatter, depending on the theoretical level (Table II). More detailed vibrational information including experimental values and those obtained by Karpfen are collected in Table VI. As a tentative conclusion the present frequencies correlate with the assignment by Karpfen but show a significant numerical error compared to the experimental data. A full and critical discussion on the experimental IR and Raman data is given by Karpfen et al.⁵⁸ Of the two possible puckered isomers of S₂N₂ with a NN or SS bridgehead bond (93 and 94) the first has been studied by Haddon et al.⁴⁵ It was shown that the energy of 93 is comparable to that of 92, and depending on the theoretical level either lower or higher in energy. In accordance with the experimental geometry larger basis set calculations place the *D*_{2h} geometry below the *C*_{2v}(4) geometry. The present calculations confirm this behavior. The 3-21G basis set predicts *C*_{2v}(4) 93 to be the lowest stationary point, although it is not a true minimum. Using the 6-31G* basis set *D*_{2h} 92 is preferred. The alternative configuration with an SS bridgehead bond is higher in energy.

Doubly protonated *D*_{2h} isomers of S₂N₂ are N₂H₂S₂²⁺ (95) and S₂H₂N₂²⁺ (100). Protonation of the nitrogen nuclei (95) results in a stable *D*_{2h} structure at all levels of theory. Compared to the neutral S₂N₂ the major change in the ring geometry is a widening of the SNS angle to approximately 100°. This results in a decreased trans annular SS repulsion. This small change in geometry is in agreement with X-ray crystallographic data on S₂N₂(SbCl₅)₂,⁶⁵ S₂N₂(AlCl₃)₂,⁶⁶ and a number of [M₂(S₂N₂)] transition-metal complexes.⁶⁷ In these compounds the substituent atoms are linked diametrically to the in-plane free-electron pairs of the nitrogen nuclei. The reported geometries all show a planar ring with an SN bond length varying from 1.62 to 1.66 Å and a widening of the SNS angle amounting to 94–96°. Apparently the coordination of the nitrogen nuclei with an electron acceptor does not significantly change the dimensions of the S₂N₂ ring. The bicyclobutane-like configurations of N₂H₂S₂²⁺ (96–99) are

stable structures at the 6-31G* level but are significantly higher in energy than planar **95**. The energy differences among the four structures (**96–99**) are relatively small with the NN bridgehead bonded $C_{2v}(4)$ isomer being slightly preferred.

Protonation of the sulfur nuclei is energetically unfavourable and the D_{2h} optimized geometry **100** possesses a number of imaginary frequencies (3-21G: B_{2g} , B_{1u} , B_{2u} and 6-31G*: B_{2g} , B_{1u}). Relaxation along the B_{2g} and B_{1u} modes using the 6-31G* basis set results in a structure of $C_s(1)$ symmetry (**101**) with an allylic SHN_2^+ fragment and a SH^+ moiety. However, this conformation is still 149 kcal/mol above (**95**) at the 6-31G* level. With respect to the puckered isomers of $S_2H_2N_2^{2+}$ the 3-21G calculations reveal a barrierless dissociation for all three possible conformations with a NN bridgehead bond (**102–104**) and a stationary point with two imaginary vibrational frequencies for the SS bridgehead bonded structure (**104**). At the 6-31G* level a dissociation is only found for the endo/endo conformation **103**, whereas the exo/exo (**102**) and endo/exo (**104**) configurations correspond to true minima. Structure **102** is the lowest in energy for the $S_2H_2N_2^{2+}$ cyclic isomers but is clearly unfavorable with respect to the planar D_{2h} tautomer **95** by 97 kcal/mol.

1.7. Oxygen–Sulfur Rings (106–108). No detailed theoretical study of the $S_2O_2^{2+}$ dication (**106**) has been published besides our preliminary SCF calculations⁴ nor is there any experimental information available. The only related work is a comprehensive theoretical study on the neutral S_2O_2 molecule (8π electrons), recently reported by Marsden and Smith.⁶⁸ The planar D_{2h} form of the neutral S_2O_2 molecule was reported to be a transition state with one imaginary out-of-plane vibrational frequency at the SCF/DZP level. The SO single bond of the optimized slightly puckered (9.8°) C_{2v} structure is 1.717 Å and the OSO and SOS angles are equal to 95.8° and 83.4° respectively. With respect to the dication (**106**) both 3-21G and 6-31G* basis sets reveal a stable D_{2h} conformation at the SCF level. MP2/6-31G* calculations confirm this conclusion. Comparing to the neutral S_2O_2 molecule the SO bond length is reduced (1.637 Å) and the OSO angle decreased to 83.0° . It is noteworthy that the frequency of the B_{3u} ring deformation rises dramatically from 301 to 1127 cm^{-1} going from SCF/6-31G* to MP2/6-31G*. Based on the calculated harmonic frequencies the D_{2h} $S_2O_2^{2+}$ dication seems a stable species, similar to the experimentally known D_{2h} S_4^{2+} dication. With respect to the puckered structures, the calculations reveal that both the OO and SS bridgehead bonded $C_{2v}(4)$ conformations (**107** and **108**) are considerably higher in energy. It is to be noted that geometry optimization at the 3-21G level of **108** within $C_{2v}(4)$ constraint results in a planar stationary point without a bridgehead bond (SS = 2.917 Å) possessing two imaginary vibrational frequencies.

1.8. Phosphorus–Sulfur Rings (109–123). The cyclic S_2P_2 (1,3,2,4-dithiadiphosphetidine), a phosphorous analogue to S_2N_2 , has not been identified experimentally. S_2P_2 has been studied at the MNDO level by Bews and Glidewell,⁶⁹ who considered three configurations: two cyclic planar structures, one with alternating atoms (PSPS, D_{2h} , $\Delta H_f^\circ = 10.7$ kcal/mol) and one with non-alternating atoms (SPPS, C_{2v} , $\Delta H_f^\circ = 15.9$ kcal/mol). The lowest-energy configuration, however, is a bicyclobutane-like $C_{2v}(4)$ geometry ($\Delta H_f^\circ = 9.4$ kcal/mol) with a PP bridgehead bond. The present calculations show that the D_{2h} geometry corresponds to a local minimum on the potential energy surface at all levels of theory. In qualitative accordance with the MNDO results the puckered $C_{2v}(4)$ conformation **110** is more stable (–13 kcal/mol at the 6-31G* level).⁶⁹ The alternative configuration with a SS bridgehead bond **111** is energetically unfavorable.

The D_{2h} optimized geometry (**112**) of the 2,4-doubly protonated 1,3,2,4-dithiadiphosphetidine, $P_2H_2S_2^{2+}$ possesses two imaginary frequencies at the 3-21G and 6-31G* levels for the B_{2g} out-of-plane and B_{1u} pucker modes. Subsequent optimization of the resulting $C_s(1)$ configuration produces a true minimum (**113**). The four possible puckered structures (**114–117**) invariably correspond to true minima (except for **117** at 3-21G) with energies

similar to that of the $C_s(1)$ geometry. At the 6-31G* level the calculations reveal: **113** ($C_s(1)$) 0.0 kcal/mol; **114** ($C_{2v}(2)$) +3.3 kcal/mol; **115** ($C_{2v}(3)$) 9.9 kcal/mol; **116** ($C_s(2)$) 5.8 kcal/mol; and **117** ($C_{2v}(4)$) 25.5 kcal/mol.

The tautomer with two protons on sulfur in stead of on phosphorus, $S_2H_2P_2^{2+}$, possesses two imaginary vibrational frequencies in the D_{2h} optimized geometry (**118**) corresponding to B_{2g} and B_{1u} modes. Subsequent geometry optimization within $C_s(1)$ constraint produces a stable minimum (**119**). At the 6-31G* level the initially imaginary pucker deformation disappears and a C_{2h} configuration is obtained. The three puckered configurations of $S_2H_2P_2^{2+}$ with a bridgehead PP bond (**120–122**) are local minima lying below $C_s(1)$ (or C_{2h}) **119**. At the 6-31G* level **119** (C_{2h}) +65.3 kcal/mol; **120** ($C_{2v}(2)$) 0.9 kcal/mol; **121** ($C_{2v}(3)$) 6.5 kcal/mol; **122** ($C_s(2)$) 1.4 kcal/mol. The $C_{2v}(4)$ SS bridgehead bonded stationary point does not represent a local minimum.

1.9. Sulfur Rings (124–125). The cyclotetrathiane dication S_4^{2+} has originally been identified by magnetic circular dichroism^{10b} and was subsequently isolated as $S_4(SO_3F)_2$ and characterized.⁷⁰ A number of X-ray crystal structures of compounds containing S_4^{2+} have shown that, in accordance with earlier evidence,^{10b,70} the S_4^{2+} dication possesses a square planar geometry. The reported SS bond length fluctuates from 1.98 Å in $(S_7I)_4S_4(AsF_6)_6$ to 2.013–2.015 Å in $S_4(AsF_6)_2 \cdot 0.62SO_2$.⁶⁵ In addition several theoretical studies have addressed the geometric and electronic structure of S_4^{2+} .^{60,72–74} In a previous study⁴ we reported the optimized structure of S_4^{2+} (**124**) at the 3-21G and 6-31G* levels. The present calculation on the MP2/6-31G* level shows that the SS bond is 2.065 Å, in fair agreement with the experimental data. D_{2h} S_4^{2+} is a stable minimum at all levels of theory. The alternative $C_{2v}(4)$ geometry **125** is considerably higher in energy and possesses two imaginary vibrational frequencies at the 3-21G level.

Discussion

One of the objectives of the present work is to come to a general understanding of the structural preferences of 1,3- $X_2Z_2Y_2Z'_2$ ring systems with potential 6π aromatic resonance stabilization. The preceding sections have shown that cyclic 1,3- $X_2Z_2Y_2Z'_2$ structures can adopt various different configurations, either with a planar, a distorted or a strongly puckered ring. Figure 5 displays the global minima for the individual compounds. In this section the results of the individual compounds will be discussed from a more general point of view, focusing on similarities.

With respect to the occurrence of 6π aromaticity in four-membered inorganic rings containing second-row atoms, the calculations show that all unsubstituted rings ($P_2N_2^{2-}$, P_2O_2 , P_4^{2-} , $S_2C_2^{2-}$, S_2N_2 , $S_2O_2^{2+}$, S_2P_2 , and S_4^{2+}) invariably possess a planar local minimum with D_{2h} or D_{4h} symmetry. The P_4^{2-} , S_2N_2 , and S_4^{2+} rings have been identified experimentally via X-ray crystallographic analysis and their structures agree with the MP2/6-31G* calculations presented. Except for $S_2C_2^{2-}$ and S_2P_2 , the unsubstituted D_{2h} or D_{4h} ring invariably represents the global minimum for a cyclic alternating arrangement of the ring elements. The stability of these unsubstituted rings stems to a large extent from the absence of a possibility for an energy-lowering B_{2g} or B_{3g} out-of-plane deformation. Therefore relaxation is limited to planar deformations or ring puckering. The force constants associated with these modes are usually higher.

In addition to the unsubstituted rings, the calculations establish that the planar D_{2h} conformations of $N_2H_2P_2$ and $N_2H_2S_2^{2+}$ also represent the global cyclic minima, resisting out-of-plane vibrations or ring deformations. Although the carbon analogues $C_2H_2P_2^{2-}$ **1** and $C_2H_2S_2$ **73** do not possess a stable D_{2h} geometry, their imaginary B_{2g} vibration results in both cases in a C_{2h} minimum (**2** and **74**) less than 2 kcal/mol below the planar configuration. The out-of-plane angle of the hydrogen nuclei in these structures is approximately 20° , demonstrating the flatness of the potential energy surface for this deformation.

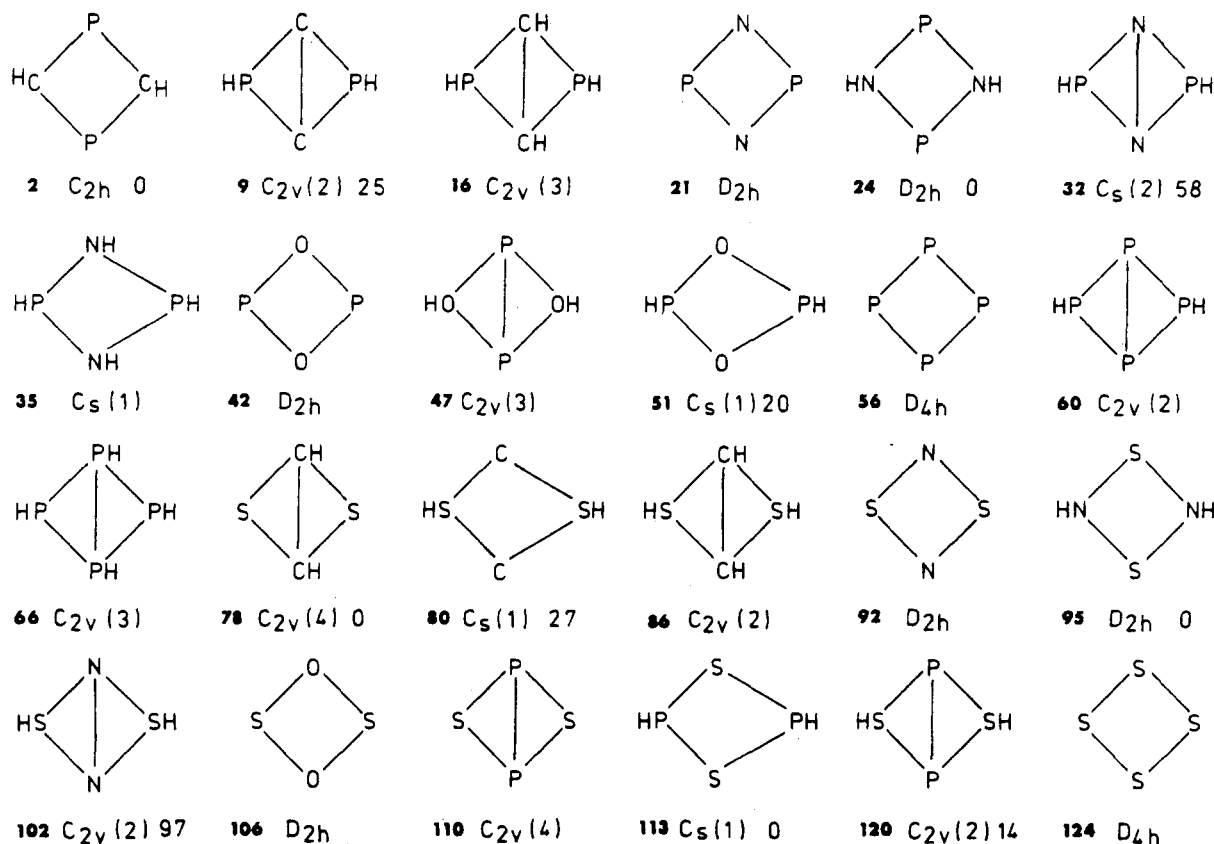


Figure 5. Schematic structures of global minima at the SCF/6-31G* level of 1,3- $X_2Z_2Y_2Z'_2$ rings. Relative energies of tautomers are given kcal/mol.

The reduced stability of the CH out-of-plane vibration compared to that of NH can be explained by the larger size of the p_z orbital of carbon compared to nitrogen. First, this results in a larger diametric repulsive interaction in the π_2 and π_3 orbitals. Second, there will be an increased overlap of the hydrogen s orbital with the p_z orbital in an out-of-plane vibration, resulting in larger stabilization. This principle can be illustrated by looking at the harmonic vibrational frequencies of the B_{2g} out-of-plane mode of the D_{2h} structures of $C_2H_2P_2^{2-}$, $N_2H_2P_2$, and $O_2H_2P_2^{2+}$ which steadily increase from 460 cm^{-1} , via 393 to 537 cm^{-1} at the 6-31G* level. As expected the vibrational frequencies of the second-row analogues P_4H_2 (779 cm^{-1}) and $S_2H_2P_2^{2+}$ (590 cm^{-1}) also increase with increasing electronegativity. An identical behaviour is found for the $X_2H_2S_2$ rings with $X = CH, NH$, and PH . The same rationale explains the result that the B_{2g} harmonic frequency is consistently larger at the 3-21G level than at the 6-31G* level with its more diffuse basis functions. It is to be noted that C_{2h} $C_2H_2P_2^{2-}$ 2 is the global minimum and the calculated ring geometries of 1 and 2 are in agreement with experimental data.¹⁴ Regarding $C_2H_2S_2$, the C_{2h} structure 74 is the global minimum at the highest theoretical level employed (MP2/6-31G*), whereas at the SCF/6-31G* level a puckered $C_{2v}(4)$ configuration) with a CC bridgehead bond prevails.

The formation of a trans-annular bond often results in a stable configuration. Within SCF/6-31G* theory several puckered structures are found that correspond to the global minimum for an alternating cyclic arrangement of ring elements: $C_{2v}(2)$ $P_2H_2C_2^{2-}$ 9; $C_{2v}(3)$ $P_2H_2C_2H_2$ 16; $C_s(2)$ $P_2H_2N_2$ 32; $C_{2v}(3)$ $O_2H_2P_2^{2+}$ 47/49; $C_{2v}(2)$ P_4H_2 60; $C_{2v}(4)$ $C_2H_2S_2$ 78; $C_{2v}(2)$ $S_2H_2C_2H_2^{2+}$ 86; $C_{2v}(2)$ $S_2H_2N_2$ 102; and $C_{2v}(2)$ $S_2H_2P_2^{2+}$ 120. It appears that these structures consistently possess a CC, NN, or PP bridgehead bond. Therefore a trans-annular bond is formed for the ring nuclei with an appreciable 1,3-overlap in π_4 . The fact that preferentially CC, NN, and PP bridgehead bonds are formed is also coherent with their larger bond energies leading to more efficient stabilization of the puckered geometries. In must be remarked that although the puckered structures of $P_2H_2C_2^{2-}$ 9, $P_2H_2N_2$ 32, and $S_2H_2P_2^{2+}$ 120 are global minima

they are higher in energy than the global minima of their tautomers viz. $C_2H_2P_2^{2-}$ 2, $N_2H_2P_2$ 24, and $P_2H_2S_2^{2+}$ 113. Derivatives of 16 and 60 are known experimentally. The available experimental geometric parameters on the 1,3-tetraphosphabicyclobutadiene derivatives are in good agreement with the ab initio results (Table V).

Finally four minima are found with a deformed $C_s(1)$ ring. These encompass $P_2H_2N_2H_2^{2+}$ 35, $P_2H_2O_2^{2+}$ 51, $S_2H_2C_2$ 80, and $S_2H_2P_2^{2+}$ 113. Structure 80 possesses an energetically favored $C_{2v}(4)$ tautomer $C_2H_2S_2$ 78.

It is tempting to formulate a guideline by which the global minima depicted in Figure 5 can be rationalized and predicted. This bypasses, however, the intrinsic fine balance of stabilizing and distortive properties that depend on the nature of the ring atoms and the presence of substituents. The following principles hold to a large extent for the different geometries at the 6-31G* level.⁷⁵ The presence of CH, PH, or SH is important. This results in an imaginary B_{2g} vibrational frequency. If these groups are absent there is a good chance that the ring will be stable in D_{2h} . When PH or SH are present, a deformation of the ring to $C_s(1)$ is very likely. The PH and SH moieties will end up in the mirror plane because of their dominant diametric repulsion in the D_{2h} geometry. However, upon deformation to $C_s(1)$ it is also important to consider the formation of a bridgehead bond between the two other members in the ring. Strong trans-annular bonds can be formed between two carbon, two nitrogen, or two phosphorus nuclei, resulting in a strongly puckered structure.

Conclusion

Using SCF/6-31G* and MP2/6-31G* calculations the conformation and stability of various 1,3- $X_2Z_2Y_2Z'_2$ derivatives has been studied in the light of potential 6 π aromaticity. A number of these compounds, their derivatives or their complexes with a transition metal are known experimentally. The present theoretical geometries consistently correspond with data from X-ray crystallography when available.

The results presented here show that the concept of resonance stabilization, in general, does not fully account for the geometric

references of 6π four-membered rings containing second-row atoms. Other effects like σ bond strength and especially energy-lowering out-of-plane distortions are at least of equal importance.^{3,4,6} A clear demonstration of this result is the fact that the theoretical ring geometries of, e.g., P_2N_2 ,¹⁸ P_4 ,²⁷ and S_2O_2 ⁶⁸ with respectively 4π , 4π , and 8π electrons are similar to their 6π electron counterparts.

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Supplementary Material Available: Tables I–IV incorporating both 3-21G and 6-31G* results (14 pages). Ordering information is given on any current masthead page.

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(75) Exceptions to this simple rationalization are the global minima **2**, **35**, **47**, **80**, and **110**. For **2** the imaginary B_{2g} mode results in a C_{2h} structure as the global minimum. C_s(1) **35** is formed because a $\equiv\text{N}^+-\text{N}^+\equiv$ bond is weaker than a $=\text{N}-\text{N}=$ bond as in **32** giving less stabilization to a puckered geometry. The D_{2h} structures of O₂H₂P₂²⁺ and S₂H₂C₂ possess an imaginary frequency for the B_{2u} mode indicating relatively weak bonds in the ring. The B_{2u} deformation in O₂H₂P₂²⁺ lowers π_4 (1,2-antibonding) more efficiently than π_3 (1,3-antibonding) resulting in the formation of a trans-annular bond as in **47**. For S₂C₂H₂ there is an additional B_{1u} imaginary vibrational frequency next to B_{2u}. This leads to pyramidalization favouring a C_s(1) geometry **80**. The C_{2v}(4) structure of S₂P₂ is most likely a consequence of the combination of the flexibility of the ring (low frequency for the B_{1u} pucker) and the PP bond strength. The puckered global minimum of S₂P₂ is 24 kcal/mol below D_{2h} S₂P₂.