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Geometrical Structures of Four Conformers of the Phosphenium Ion, $P(C_5H_5)_2^+$. A Phosphorus Sandwich?

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Abstract: Nonempirical quantum mechanical methods have been applied to the determination of the molecular structure of the title compound, the PCp_2^+ cation. Complete theoretical structures have been obtained for four distinct conformers displaying different modes of phosphorus–ring binding and lying within an energy range of 25 kcal mol⁻¹. The conformer which lies lowest in energy has only a single plane of symmetry; one C_5 ring is bound to phosphorus through a single carbon atom (η binding) and the other through two, equidistant, carbon atoms (η^2 binding). About 9 kcal mol⁻¹ higher in energy is a C_2 structure in which the phosphorus adopts η^2 coordination to both rings. About 25 kcal mol⁻¹ higher in energy are two structures of higher symmetry (namely C_{2v}) which in some respects resemble more traditional bent sandwich compounds. Several similarities and differences are noted between the lowest energy structure of the present $P(C_5H_5)_2^+$ and the recently observed $As(C_5Me_5)_2^+$, for which Jutzi and co-workers have determined a crystal structure.

Since the structural identification of ferrocene in 1952, the metallocenes MCp_2 ($Cp = C_5H_5$) have played an important role in organotransition-metal chemistry.¹ Less widely appreciated have been the main group cyclopentadienyl sandwiches, the first of which was plumbocene, synthesized in 1956 by Fischer and Grubert.² After considerable early controversy²⁻⁶ it was eventually established⁷ that $Pb(C_5H_5)_2$ in the solid state has a polymeric zigzag chain structure with bridging cyclopentadienyl rings. However, in the gas phase the electron diffraction studies of Almenningen and co-workers⁸ show plumbocene to be a bent sandwich with a ring normal–Pb–ring normal (in Almenningen's analysis this was also the ring centroid–Pb–ring centroid angle) angle of $135 \pm 15^\circ$, which corresponds to an angle between ring planes of $45 \pm 15^\circ$. It should be mentioned that the permethylated compound $Pb(C_5Me_5)_2$ has recently been synthesized and characterized crystallographically by Atwood, Hunter, Cowley, Jones, and Stewart.⁹

The lighter but valence-isoelectronic stannocene molecule, $SnCp_2$, is also well-known and preliminary electron diffraction studies by Almenningen in 1967 suggested⁸ a bent sandwich with a Cp–Sn–Cp angle of $\sim 125^\circ$ or an angle between rings of $\sim 55^\circ$. Much more recently, Atwood and co-workers⁹ determined the crystal structure of bis(cyclopentadienyl)tin and found it to be monomeric in the solid state, unlike plumbocene. There are two different ring centroid–Sn–ring centroid angles in the unit cell of stannocene and these were reported⁹ to be 148.0° and 143.7° , respectively. An alternative representation of the stannocene structure involves the angle between Cp ring planes, and Almlöf¹¹ has deduced values of 48.4° and 45.9° for the two such unique angles from the atomic coordinates reported by Atwood et al.⁹

The lightest of the known group 14²⁸ sandwich compounds, germanocene, was prepared by Scibelli and Curtis¹⁰ in 1973. There is no gas-phase molecular structure yet for $Ge(C_5H_5)_2$, but the closely related $Ge(C_5H_4Me)_2$ has an angle between ring planes of $34 \pm 7^\circ$. Very recently, a crystal structure for the parent germanocene has been reported¹² and is monomeric with the angle of aperture of the Cp rings 50.4° . In the latter structure, there is a significant range of Ge–C distances, from 2.347 to 2.730 Å. The silicone compound $Si(C_5H_5)_2$ has, to our knowledge, not yet been synthesized.

The characterization of the group 14 cyclopentadienyl sandwich compounds logically suggests the possibility of the existence of the analogous group 15 cations, namely, $P(C_5H_5)_2^+$, $As(C_5H_5)_2^+$, $Sb(C_5H_5)_2^+$, and $Bi(C_5H_5)_2^+$. This idea has been pursued experimentally with considerable success by the groups of Cowley and Jutzi. In 1981 Baxter, Cowley, and Mehrotra¹³ synthesized

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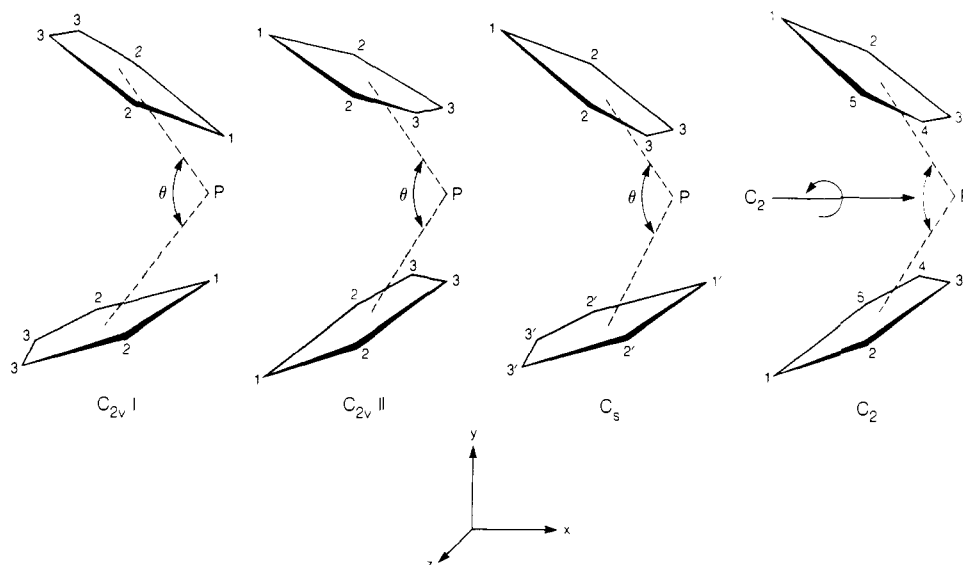


Figure 1. Qualitative depiction of the four different structures considered for the phosphocenium ion $P(C_5H_5)_2^+$. Note that equivalent atoms are given the same numerical designation.

the $[As(C_5H_5)(C_5Me_5)^+][AlCl_4^-]$ species and suggested a bent sandwich structure from the observed NMR and from model MNDO calculations. Two years later Jutzi, Wippermann, Krüger, and Krauss¹⁵ synthesized both the $As(C_5Me_5)_2^+$ and $Sb(C_5Me_5)_2^+$ cations and reported a crystal structure for the former. As expected, $As(C_5Me_5)_2^+$ is a bent sandwich, and its angle between Cp ring planes is 36.5° . Quite a range of As–C bond distances is reported by Jutzi, from 2.19 to 2.67 Å for the upper Cp ring in their figure and from 2.26 to 2.74 Å for the lower ring. On this basis Jutzi argues that the upper ring is bound in a η^3 manner and the lower ring via η^2 coordination. It is interesting to note that a molecule seemingly as symmetrical as $As(C_5Me_5)_2^+$ has only a single plane of symmetry.

Theoretical Approach

In this research we report complete theoretical structures (all geometrical parameters vigorously optimized) for conformers of the model system $P(C_5H_5)_2^+$. Cowley and co-workers^{13,14} have previously assumed that $P(C_5H_5)_2^+$ is a reasonable model for species such as $As(C_5Me_5)_2^+$, and we concur in this judgment. It is hoped that this research will serve as an impetus for further experimental studies of the group 15 cations MCp_2^+ and their derivatives.

The potential energy surface for internal rotation of the two cyclopentadienyl rings in $P(C_5H_5)_2^+$ is expected to be complicated, given Jutzi's experimental finding that $As(C_5Me_5)_2^+$ has only a single plane of symmetry. In this research we have restricted ourselves to four well-defined models, which may be represented schematically by the following:

Structure I: This is a C_{2v} structure, which may be labeled "point-to-point" in the sense that the two Cp rings approach most closely via the unique carbon atoms (atom 1 in Figure 1) of each ring. This arrangement of the C_5H_5 rings with respect to each other is observed,¹⁶ for example, in the neutron diffraction structure of $H_2Mo(Cp)_2$. In their semiempirical theoretical studies of stannocene, Baxter, Cowley, Lasch, Lattman, Sharum, and Stewart¹⁴ (see their Figure 1) assume such a point-to-point conformation.

Structure II: This is also a C_{2v} structure and may be labeled "edge-to-edge" since the point of closest approach of the Cp rings

involves the four equivalent carbon atoms (labeled 3 in Figure 1). Experimental examples of this Cp–Cp arrangement include the X-ray structure of $H_3Nb(Cp)_2$ and the neutron-diffraction structure of $H_3Ta(Cp)_2$ reported by Bau and co-workers¹⁷ and the $(CO)_2Ti(Cp)_2$ X-ray structure of Atwood and co-workers.¹⁸ Such an edge-to-edge structure has frequently been assumed in model theoretical studies.^{19–21}

Structure III: Having only a plane of symmetry, this conformation may be designated "point-to edge" in the notation developed above. The $As(C_5Me_5)_2^+$ structure of Jutzi and co-workers¹⁵ falls in this category, as do several of the earlier crystal structures of Prout and co-workers.²²

Structure IV: Closely related to the C_{2v} structure II, this conformation relaxes (i.e., removes) the equivalence between atoms 2 and 5 and between atoms 3 and 4. Thus the only nontrivial element of symmetry is the twofold rotation axis seen in Figure 1.

The four structures were optimized via analytic gradient methods by using one of the simplest ab initio theoretical models potentially suitable for this problem. The self-consistent-field (SCF) method was used in conjunction with the standard minimum basis set recommended by Pople and co-workers.²³ This basis set was augmented by a set of d functions (orbital exponent $\alpha = 0.39$) centered on the phosphorus atom, and the composite basis is designated STO-3G*. As reported elsewhere, d function utilization in compounds of this type tends to be exaggerated in supplemented minimal basis set calculations.²⁴ Optimized structures determined at this level depart more from experiment than do structures obtained with extended basis sets supplemented with d functions but are still better than structures obtained without the addition of the higher order functions.

Although the number of basis functions is not large (75 contracted Gaussian functions), the number of nuclear degrees of freedom is substantial, $3N - 6$ for $N = 21$ being 57. The phosphocenium ion is thus one of the larger unsymmetrical molecular

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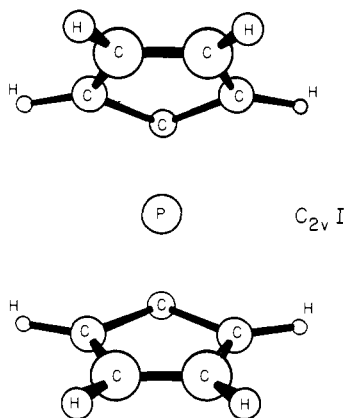


Figure 2. Structure I for P(C₅H₅)₂⁺, also designated "point-to-point". Numerical values of the predicted bond distances and bond angles are given in Table I.

Table I. Predicted Geometrical Parameters for Four Conformations of P(C₅H₅)₂⁺^a

	I (C _{2v})	II (C _{2v})	III (C _s)	IV (C ₂)
P-ring 1 centroid	2.077	2.056	2.118	2.169
P-ring 2 centroid	2.077	2.056	2.622	2.169
X-P-X angle θ (X = ring centroid)	170.8	167.5	157.4	166.8
ring normal-P-ring normal angle φ	119.1	109.5	69.2	95.4
angle between Cp rings	60.9	70.5	110.8	84.6
P-C distances				
P-C ₁	1.828	2.835	1.816 (3.011)	1.807
P-C ₂	2.258	2.541	2.675 (2.641)	2.105
P-C ₃	2.766	1.944	3.482 (1.860)	2.775
P-C ₄	2.766	1.944	3.482 (1.860)	3.004
P-C ₅	2.258	2.541	2.675 (2.641)	2.561
C-C distances				
C ₁ -C ₂	1.485	1.391	1.527 (1.391)	1.513
C ₂ -C ₃	1.375	1.434	1.324 (1.462)	1.374
C ₃ -C ₄	1.421	1.484	1.484 (1.503)	1.446
C ₄ -C ₅	1.375	1.434	1.324 (1.462)	1.347
C ₅ -C ₁	1.485	1.391	1.527 (1.391)	1.499
C-H distances				
C ₁ -H ₁	1.083	1.081	1.090 (1.081)	1.085
C ₂ -H ₂	1.083	1.087	1.081 (1.093)	1.080
C ₃ -H ₃	1.083	1.081	1.083 (1.083)	1.088
C ₄ -H ₄	1.083	1.081	1.083 (1.083)	1.081
C ₅ -H ₅	1.083	1.087	1.081 (1.093)	1.085

^a See Figure 1 for numbering of the different carbon atoms. Hydrogen atoms are numbered according to the carbon atoms to which they are bonded. Bond distances are in angstroms and angles are in degrees. For structure III only, the upper and lower cyclopentadienyl rings are inequivalent; distances in parentheses refer to the lower Cp ring of Figure 4.

species for which complete theoretical structures have been obtained for more than a single conformer.

Once the four STO-3G* SCF structures were obtained, single point SCF wave functions and energies were determined by using a much larger double-ζ (DZ) basis set, again augmented by a set of phosphorus d functions (α = 0.50). The standard Huzinaga-Dunning-Hay contracted Gaussian basis sets^{25,26} were used, designated P(11s7p1d/6s4p1d), C(9s5p/4s2p), and H(4s/2s). This larger basis set may be seen to include 144 contracted Gaussian functions; geometry optimization at this level was not feasible.

Four Conformations of P(C₅H₅)₂⁺ Energetics

The four theoretical structures for the phosphocenium ion are seen in Figures 2-5, with precise geometrical parameters given

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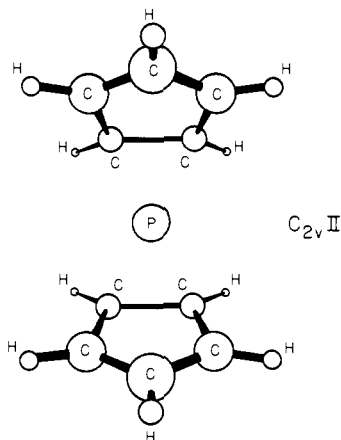


Figure 3. Structure II for P(C₅H₅)₂⁺, also designated "edge-to-edge". Geometrical parameters are given in Table I.

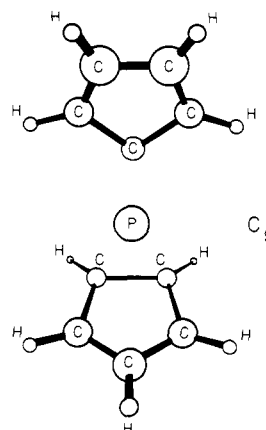


Figure 4. Structure III for P(C₅H₅)₂⁺, also designated "point-to-edge". Structural parameters are summarized in Table I.

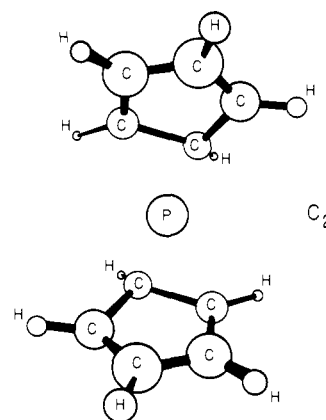


Figure 5. Structure IV for P(C₅H₅)₂⁺. Theoretical bond distances and angles are given in Table I.

Table II. Absolute Energies (hartrees) and Relative Energies (kcal mol⁻¹) for the P(C₅H₅)₂⁺ Structures Illustrated in Figures 2-5

	STO-3G* SCF		DZ+d SCF	
	absolute	relative	absolute	relative
structure I (C _{2v}) (point-to-point)	-716.59021	14.1	-724.74081	22.9
structure II (C _{2v}) (edge-to-edge)	-716.59410	11.6	-724.73739	25.0
structure III (C _s) (point-to-edge)	-716.61266	0.0	-724.77726	0.0
structure IV (C ₂)	-716.60591	4.2	-724.76299	9.0

in Table I. The predicted absolute and relative energies of the four conformers are set out in Table II.

Since it is desirable to place greatest emphasis on the lower energy structures, the present discussion begins with an assessment of the energetics reported in Table II. It must be noted immediately that the structures of the four conformers were optimized at the STO-3G* SCF level of theory only. The DZ+d SCF entries in Table II assumed the geometrical parameters predicted at the less complete STO-3G* level of theory.

Structure III, the C_s or point-to-edge structure, is calculated to lie lowest in energy, followed by structure IV, the C_2 conformer. This conclusion is obtained at both basis set levels, the energy difference between structures III and IV being 4.2 kcal mol⁻¹ with the STO-3G* basis set and 9.0 kcal mol⁻¹ with the larger DZ+d basis.

The higher symmetry structures I and II lie much higher in energy. Again the result is the same at both basis set levels, and again the smaller basis yields the smaller energy difference. At the fully optimized STO-3G* level, structures I and II lie 14.1 and 11.6 kcal mol⁻¹, respectively, above the lowest energy structure III. With the DZ+d basis set, the energies of structures I and II are 22.9 and 25.0 kcal mol⁻¹ above that of structure III. Geometrical optimization at the DZ+d SCF level would undoubtedly change these energies somewhat, but one might speculate that the less symmetrical structures III and IV, with about twice as many independent geometrical parameters, would benefit more in energy than the C_{2v} structures I and II. We conclude that the significant energy difference between structure III and the higher-lying structures I and II is genuine.

It would, of course, be desirable to consider the effects of electron correlation on the relative energies of the different P-(C₅H₅)₂⁺ structures. Unfortunately this is beyond the scope of the present research. In general one expects correlation effects on such an internal rotation potential energy surface to be small, but this is much more a hope than a certainty.

Structural Features of P(C₅H₅)₂⁺

The emergence of structure III, the C_s or "point-to-edge" structure, as the lowest in energy, necessitates some further discussion. Most obvious is the observation that the theoretical lowest energy structure for the model compound P(C₅H₅)₂⁺ falls in the same point group as the observed crystal structure for the valence isoelectronic molecule As(C₅Me₅)₂⁺, synthesized by Jutzi's group.¹⁵ Moreover, As(C₅Me₅)₂⁺ has a similar "point-to-edge" structure as P(C₅H₅)₂⁺. Perhaps the biggest difference between the arsenic and phosphorus structures occurs for the angle between cyclopentadienyl rings. Such an angle must be defined for PCp₂⁺ in some average sense, since the five cyclopentadienyl carbon atoms do not fall on a plane for any of the structures considered here. In this work, the term "Cp ring plane" always refers to the "best" plane as determined by a least-squares fit.

The angle between Cp rings is 36.5° for As(C₅Me₅)₂⁺, but it is predicted to be much greater, 110.8°, for P(C₅H₅)₂⁺. We must note that CH₃-CH₃ hindrance between rings in the arsenic compound is at least partly responsible for the difference. The effect is well-known and has been demonstrated rather dramatically during the past year by the finding²⁷ that decaphenylstannocene Sn(C₅Ph₅)₂ has a D_{5d} crystal structure, i.e., angle between ring planes = 0.0°. As discussed in our introduction, for the unsubstituted stannocene Sn(C₅H₅)₂, the observed angles between ring planes are 46° and 48°. The importance of steric effects on the structures of main group sandwich compounds is obvious.

Jutzi, Wipferman, Krüger, and Krauss¹⁵ state that As-(C₅Me₅)₂⁺ displays η^2 and η^3 coordination, rather than the ideal η^5 bonding to the central As atom. It is of interest to see if this

is true as well for the theoretical structure of the lowest energy conformer of P(C₅H₅)₂⁺. For the upper C₅ ring of the arsenic cation, Jutzi report As-C distances of 2.19, 2.38 (two of these), and 2.66 Å (two). For P(C₅H₅)₂⁺ (structure III), the P-C distances seen in Table I are 1.82, 2.68 (two), and 3.48 Å (two). These distances may be compared with the optimized P-C distance in methyl phosphine of 1.84 Å predicted at the same level of theory.²⁴ Experimental P-C bond lengths for P(III) compounds lie generally in the range 1.83–1.85 Å with shorter values only for groups capable of supporting multiple bonding between carbon and phosphorus. Hence for P(C₂H₅)₃ and P(CN)₃ the P-C bond lengths drop to 1.75 and 1.79 Å, respectively. Aided by this comparison we predict the coordination of the phosphorus cation to be η or (less realistically) η^3 , but certainly not η^5 .

For the lower ring of the arsenic compound, As-C distances reported by Jutzi¹⁵ are 2.26 (two), 2.56 (two), and 2.74 Å. The analogous distances for P(C₅H₅)₂⁺ are 1.86 (two), 2.64 (two), and 3.01 Å. Thus the tendency away from η^5 coordination for As-(C₅Me₅)₂⁺ is predicted to be much more striking for the model cation P(C₅H₅)₂⁺. In our opinion the phosphorus-ring bonding in the latter species is best described in terms of η and η^2 coordination.

Structure III, the lowest lying energetically of the four conformers of P(C₅H₅)₂⁺ considered here, is in a sense the most spatially extended of the four structures. The sum of the two phosphorus-ring centroid distances is 4.74 Å for structure III, as compared to 4.34 Å for structure IV, and even smaller values for structures I and II. Further, structure III is the "most bent" of the four conformations, with a ring centroid-P-ring centroid angle of 157.4°, vs. 166.8° for structure IV.

The characterization of structures I, II, and IV in terms of coordination to the central phosphorus is of some interest. Structure IV, lying next energetically above III, has P-C distances of 1.81, 2.11, 2.56, 2.78, and 3.00 Å, with each P-C distance occurring once to the upper ring and once to the lower ring. Thus both rings are bound η^2 to the central phosphorus. Turning to structure I, it displays P-C distances of 1.83, 2.26 (two to each Cp ring), and 2.77 Å (two to each Cp ring). Thus structure I could be labeled η for both rings or η^3 for both rings. Structure II by the same standard has two short P-C distances (1.94 Å) for each ring and is best identified as η^2 with respect to both rings.

The ring carbon-carbon distances show quite significant variations between the four conformers. The lowest energy structure III shows substantial alternation in its upper ring C-C distances, predicted to be 1.32 (two), 1.48, and 1.53 Å (two). Since the first and last of these fall nicely in the established range of C=C double and C-C single bond distances, one may sketch the upper ring structure as



Note of course that the two equivalent C-C single bonds share the carbon atom bound η to the central phosphorus atom. For the lower Cp ring in structure III, the carbon-carbon distances show lesser variation, being 1.39 (two), 1.46 (two), and 1.50 Å. A rough valence structure for the lower ring might accordingly be



As expected from our earlier characterization of the lower Cp ring as η^2 to the phosphorus atom, the C-C single bond in the above sketch lies closest to the central phosphorus atom.

Since the present P(C₅H₅)₂⁺ species is notably more bent than the observed As(C₅Me₅)₂⁺, we expect the latter to display less variation in carbon-carbon distances within the Cp rings. This turns out to be true, with Jutzi's crystal structure¹⁵ displaying C-C distances of 1.40, 1.42 (two), and 1.45 Å (two) in the upper ring, with 1.41 (two), 1.42 (two), and 1.44 Å in the lower ring. As with the theoretical predictions for P(C₅H₅)₂⁺, the crystal

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(28) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

structure for the arsenic compound shows those carbon atoms to be most nearly saturated (as demonstrated by longer bonds to adjacent carbon atoms) that are most closely coordinated to the central arsenic atom.

We note finally that the more symmetric C_{2v} structures I and II show much less variation in C-C bond distances. For structures I and II the ranges of C-C distances are 0.11 and 0.09 Å, respectively, as compared to 0.20 Å for the lower energy structure III. This is of course consistent with the smaller range of P-C distances predicted for structures I and II.

Concluding Remarks

Complete theoretical structures have been predicted for four distinct conformers of the $P(C_5H_5)_2^+$ molecular ion. The theoretical energy differences suggest that separate identification of conformers of compounds of this class ought to be possible with techniques such as variable-temperature NMR. The lowest energy structure displays only a single plane of symmetry and is in some respects qualitatively similar to the crystal structure of $As(C_5Me_5)_2^+$, reported in 1983 by Jutzi, Wippermann, Krüger, and Krauss.¹⁵ The theoretical phosphorus structure, due in part to the absence of hindrance from methyl substituents on the Cp rings, is significantly more bent than the permethylated arsenic compound. Similarly, the phosphorus cation displays much more variation of the carbon-carbon bond distances within the Cp rings than does the arsenic structure. To the extent that Jutzi and co-workers are justified in labeling $As(C_5Me_5)_2^+$ as η^2 and η^3 with respect to the central arsenic atom, the lowest energy $P(C_5H_5)_2^+$

structure is best described as involving η and η^2 coordination. C-C distances in both rings are consistent with the electron distribution in the ring implied by these two types of interaction (P-C single bonding and three-center P-C₂ bonding, respectively); the same is true of the C-C distances and P-ring interactions in the three higher-energy conformations.

Since structure III of Figure 1 has the lowest energy for all levels of theory considered in this study, it is of interest to note that the HOMO (highest occupied molecular orbital) is an a'' orbital essentially concentrated in the lower ring and involving the $2p_x$ and $2p_y$ atomic orbitals (the xy plane is the plane of symmetry) of the 2' and 3' carbon atoms. The LUMO (lowest unoccupied molecular orbital), on the other hand, is an a'' orbital involving principally the phosphorus $3p_z$ orbital and the $2p_x$ and $2p_y$ atomic orbitals of the upper ring carbon atoms labeled by 2 in Figure 1. Apart from the phosphorus core orbitals (1s, 2s, and 2p), which are all very low lying, there are no MOs uniquely associated with phosphorus and hence no canonical MO which could be described as a phosphorus lone pair.

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Does Fluoroformic Acid Exist?

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Abstract: This study was carried out for three reasons. The ab initio MO method is used for prediction of the existence of fluoroformic acid as an isolated species, arguments are given to explain the failure to synthesize this substance, and, finally, a previously reported potential energy surface for the van der Waals region of the $CFHO_2$ system is extended into the region of the bonded $CFHO_2$ molecule. The isolated fluoroformic acid molecule is found to be a stable species with a relatively high barrier for unimolecular decomposition into CO_2 and HF (210 kJ/mol), corresponding to a symmetry-forbidden-like reaction. In a protic medium fluoroformic acid decomposes with a low barrier, as indicated by the MNDO method. Cis and trans minima were found for the acid, as well as a saddle point for internal rotation. Infrared spectra were calculated for both conformers and vibrational analysis was performed for the transition states of internal rotation and dissociation processes.

Elementary textbooks of organic and inorganic chemistry generally state that the monofluoro derivative of carbonic acid does not exist because it decomposes immediately into CO_2 and HF (e.g., ref 1). The fluoride of carbonic acid, fluoroformic acid, $FCOOH$, is nevertheless mentioned in the literature. Attempts to isolate fluoroformic acid were usually carried out in aqueous solutions. Gordon and Lin² have studied the laser-induced reaction of $:CHF + O_2$. They proposed the formation of vibrationally excited fluoroformic acid and its unimolecular decomposition into CO_2 and vibrationally excited HF. They assumed a very low

activation energy for the unimolecular process in analogy to the observed activation energy of 54 kJ/mol for the related reaction, $ClCOOH \rightarrow HCl + CO_2$, studied by Jensen and Pimentel.³ However, the decay of chloroformic acid represents only one branch of a suggested mechanistic scheme of the radical photo-reaction of chlorine with formic acid. Thus, the observed activation energy may not correspond to the monomolecular decomposition of chloroformic acid.

Cremer⁴ has performed calculations for the ozonolysis of fluoroalkenes via the Criegee path.⁵ He assumed the formation of fluoroformic acid during hydrolysis of the final ozonide and calculated the energy of fluoroformic acid at its standard geometry

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