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systems where the ground state of the π cation radical has been experimentally determined. The method was then used to determine the effect of substituents in cases where the ground state is unknown. Meso substituents that are electron donating lead to a 2A1u ground state, while those that are electron withdrawing lead to a 2A1g ground state. The β-substituted porphyrins maintained the 1A1g π cation radical ground state of the unsubstituted porphyrin and have a smaller effect on the relative energies of the 2A1g and 3A1g states compared to the meso substituents. Multivariate linear regression analyses, reflecting basic electronic principals, indicate that a balance between π effects, which tend to destabilize the aπ1 and aπ2 orbitals, and σ effects, which generally stabilize the orbitals, can explain the state energy orderings of the substituted Mg(II) porphyrins studied here. These states can be distinguished by experimental techniques such as NMR, EPR, and ENDOR that monitor the extent of unpaired spin on the substituents and porphyrin ring atoms. Since protoporphyrin IX, the most commonly occurring porphyrin group in endogenous heme proteins, does not have meso substituents but has only β substituents, as do all the other naturally occurring porphyrins found in heme proteins, it would be expected to form 1A1g π cation states in the four-coordinate Mg(II) case. However, substitution of Fe for Mg and addition of axial ligands can be further modulators of these states and can lead to different ground states and properties. Future studies will address the role of these additional factors in determining the nature and selective stability of their π cation states.

Acknowledgment. We would like to thank Drs. Ping Du and Jack Fajer for helpful discussions during the course of this study. Support from the National Science Foundation (Grant No. DMB-9096181) for this work is gratefully acknowledged.

Ab-Initio Calculations on Vibronic Coupling in the Lower Triplet States of Pyrimidine

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Abstract: Ab-initio calculations at the UHF and CASSCF levels have been performed in which the geometry of pyrimidine in the 1B1u(π*), 1A2u(π*), and 1A2u(ππ*) states has been optimized. The calculations clearly demonstrate the influence of vibronic coupling on the molecular and electronic structure of the molecule in these states. For the ππ* states, conformations corresponding to minimum energy are found that deviate significantly from planar. For the 1A2u(ππ*) state, vibronic coupling similar to that between the 1B1u and 1E1u states of benzene has been found. From the calculations, we deduce a dynamic out-of-plane distortion of the molecule in the 1B1u(π*) state, which provides for a coherent description of the results of optical and magnetic-resonance data available for the lowest triplet state of pyrimidine. The out-of-plane distortions occurring in the 1B1u(π*) and 1A2u(ππ*) states conform to the increased antibonding character of the π-electron system upon ππ* excitation.

Introduction

The class of azaaromatic molecules distinguishes itself from the hydrocarbon analogues by the presence of one or more nitrogen atoms in the conjugated system. The introduction of these nitrogen atoms leads to the occurrence of ππ* excited states and modifies the electronic properties of the ππ* excited states as compared to those of their hydrocarbon parent compounds. Extensive experimental and theoretical studies have been performed to characterize the low-lying excited states of azaaromatic compounds, as amply illustrated in a recent review.1 For many such molecules, vibronic coupling has been invoked between nπ* and ππ* states as well as among ππ* states in order to describe the properties of the excited states.

For pyridine, the simplest azaaromatic molecule, such studies have been problematic for a long time owing to its unfavorable emissive characteristics. Recently, we were able to unravel in great detail the molecular and electronic structure of pyridine in the lowest triplet state (3B1u(π*) by the application of electron spin echo (ESE) spectroscopy2†and by ab-initio calculations.6 From the observed nitrogen and deuterium hyperfine interactions, it was found that pyridine upon excitation adopts a boatlike structure in which the nitrogen and the para-carbon atoms are tilted by about 40° and 10°, respectively, with respect to the plane spanned by the ortho- and meta-carbon atoms. The nonplanar structure could be rationalized in terms of a strong vibronic coupling between the 1B1u(π*) and 1A2u(ππ*) states. In agreement with the vibronic coupling picture, the observed spin-density distribution reflected a state of both nπ* and ππ* character.

The experimentally determined molecular structure has subsequently been confirmed by theoretical studies performed by Nagaoka and Nagashima7 and by us.4 From our calculations, we concluded that the observed distortion could, besides in terms of vibronic coupling, be considered in terms of the increased antibonding character of the π-electron system upon ππ* excitation. This suggested that the π* orbital involved in the excitation might determine the character of the geometry relaxation. Indeed, our calculations showed that the nodal-plane structure of the 3B1u(π*) orbital correlates very well with the way pyridine distorts in the lowest triplet state.

Vibronic Coupling in Pyrimidine

Apart from the vibronic coupling with \( \pi^* \) states, the \( \pi \pi^* \) triplet states in azabenzene may be subject to vibronic coupling with other \( \pi \pi^* \) triplet states. In azabenzene, a low-lying \( \pi \pi^* \) triplet state is present which is the analogue of the \( \text{B}_1 \) state of benzene. This state has both experimentally\(^1\)\(^-\)\(^12\) and theoretically\(^1\)\(^-\)\(^19\) been shown to be subject to a large vibronic coupling with the \( \text{E}_1 \) state of common MO parentage. As the result of this vibronic coupling, benzene in the \( \text{B}_1 \) state is not stable in the \( D_8h \) conformation but distorts along the two-dimensional \( e_\text{g} \) vibrational coordinate \( \nu_1 \) in such a way that the potential energy surface of the \( \text{B}_1 \) state exhibits a Mexican hat shape along \( \nu_2 \). Within the trough of this surface, three equivalent minima and three equivalent saddle points can be found which correspond to quinoidal and anti-quinoidal conformations. Recently, we investigated by ab-initio calculations the shape of the potential energy surface of the \( \text{B}_1 \) state along the \( e_\text{g} \) symmetry coordinate \( S_{(\rho,\phi)} \)\(^1\)\(^-\)\(^19\). The energy variation within the trough, i.e., the energy difference between quinoidal and anti-quinoidal conformations, is found to be negligible compared to the stabilization energy that is gained by the distortion of the molecule from \( D_8h \) symmetry. Additionally, the calculation of vibronic energy levels and crystal field supported the idea that the distortion of benzene in the \( \text{B}_1 \) state is not a static process but a dynamical one.

In the present paper, we are concerned with the lower triplet states of pyrimidine (1,3-diazabenzene). By ab-initio calculations, we investigate the influence of vibronic coupling on the geometric and electronic structure of pyrimidine in the \( \text{B}_1(n\pi^*) \), \( \text{A}_1(n\pi^*) \), and \( \text{A}_2(n\pi^*) \) states. The most relevant molecular orbitals for the description of these states are schematically indicated in Figure 1. The \( \text{B}_1(n\pi^*) \) state can in first approximation be represented by the configuration \( \{7b_2(n^*) \rightarrow 2a_2(\sigma^*)\} \), the \( \text{A}_1(n\pi^*) \) state by \( \{7b_2(n^*) \rightarrow 3b_1(\pi^*)\} \), and the \( \text{A}_2(n\pi^*) \) state by a mixture of the \( \{1a_2(\pi^*) \rightarrow 2a_1(\sigma^*)\} \) and \( \{2b_1(\pi^*) \rightarrow 3b_1(\pi^*)\} \) configurations. The results of the calculations on the \( n\pi^* \) states will be compared with those obtained for the lower triplet state of pyridine. Especially interesting is the fact that the same \( \pi \pi^* \) orbital is involved in the excitation to the \( \text{A}_2(n\pi^*) \) state of pyridine as to the \( \text{B}_1(n\pi^*) \) state of pyrimidine. The \( \text{A}_1(n\pi^*) \) state, on the other hand, is the analogue of the \( \text{B}_1 \) state of benzene. Calculations on this state allow for a discussion of the influence of the nitrogen atoms in the aromatic system on the vibronic coupling between \( \pi \pi^* \) states.

The present calculations are of interest not only from a theoretical point of view but also in relation to the results of spectroscopic studies. Pyrimidine has a large phosphorescence quantum yield, and the lowest triplet state, \( \text{B}_1(n\pi^*) \), has consequently been extensively studied by optical spectroscopy and optical detection of magnetic resonance. For the triplet manifold, vibronic coupling has repeatedly been invoked in order to explain experimental observations. The most salient among these observations concern the populating rates and the emission spectra of the sublevels of the lowest triplet state. Burland and Schmidt have observed that the populating rate of the \( T_1 \) sublevel related to the out-of-plane axis is anomalously high.\(^20\) Inoue and Lim rationalized this result by assuming a pseudo-Jahn–Teller distortion of pyrimidine in the \( \text{A}_1(n\pi^*) \) and/or the \( \text{B}_2(n\pi^*) \) state caused by a strong vibronic coupling with the \( \text{A}_2(n\pi^*) \) state.\(^21\) In addition, these authors suggested that the prominent presence of totally-symmetric bands in the emission spectrum of the \( T_1 \) sublevel, which would be forbidden for a molecule of \( C_2 \) symmetry, is induced by an interplay of vibronic interactions and an anisotropic crystal field.\(^21\) Hereby the molecule would acquire a symmetry lower than \( C_2 \) in the \( \text{B}_1(n\pi^*) \) state. Nonhof and van der Waals inferred a similar symmetry lowering from optically-detected magnetic-resonance experiments in a magnetic field\(^22\)\(^-\)\(^23\) and suggested vibronic coupling between the \( \text{B}_1(n\pi^*) \) and \( \text{A}_2(n\pi^*) \) states. Finally, the study of the polarization of bands in the \( T_1 \) sublevel phosphorescence spectrum led Umemoto et al. to the conclusion that pyrimidine in the \( \text{B}_1(n\pi^*) \) state is distorted along a \( b_1 \) vibrational coordinate, yielding a molecule of \( C_{1h} \) symmetry.\(^23\) On the other hand, Donckers et al. concluded from a study of the nitrogen and proton hyperfine interactions in the \( \text{B}_1(n\pi^*) \) state of pyrimidine present as a guest in a single crystal of benzene-\( d_6 \) that pyrimidine shows up as a planar molecule in the \( \text{B}_1(n\pi^*) \) state on the time scale of their optically detected electron nuclear double resonance (ODENDOR) experiments.\(^26\) They found no evidence for vibronic coupling with higher lying \( \pi \pi^* \) states.

In our calculations, we have optimized the geometry of pyrimidine in the triplet states at the unrestricted Hartree–Fock (UHF) as well as the complete active space self-consistent field (CASSCF) level. The motivation for performing these two types of calculations stems from previous studies on the \( \text{B}_1(n\pi^*) \) state of pyridine.\(^6\)\(^7\) For this state, a qualitatively correct picture of the dominant geometry changes induced by the excitation was obtained already at the UHF level. The geometry optimizations of pyrimidine in the \( \text{B}_1(n\pi^*) \), \( \text{A}_1(n\pi^*) \), and \( \text{A}_2(n\pi^*) \) states demonstrate that vibronic coupling is prominently present in the lower triplet manifold. The \( \text{B}_1(n\pi^*) \) state is vibronically coupled to the \( \text{A}_1(n\pi^*) \) state and has a nonplanar configuration at an energy of 68 cm\(^{-1}\) below that of the planar conformation. The \( \text{A}_1(n\pi^*) \) state is even more perturbed by vibronic coupling with the \( \text{B}_2(n\pi^*) \) state, resulting in an energy minimum for a nonplanar configuration at about 500 cm\(^{-1}\) below the planar conformation. The \( \text{A}_2(n\pi^*) \) state exhibits similar in-plane deformations as previously encountered in the \( \text{B}_1 \) state of benzene, albeit that the energy variations in the trough are considerably larger than the ones calculated for benzene. On the basis of the present calculations, we conclude that there is a dynamic out-of-plane distortion of pyrimidine in the lowest triplet state. Such a view offers a coherent explanation for the seemingly contra-
dictory results of optical and magnetic-resonance experiments. Finally, the calculated conformational behavior of pyrimidine in the \( ^3B_1(n^*) \) and \( ^3A_2(n^*) \) states will be considered in relation to previous theoretical results on the \( ^3B_1(n^*) \) state of pyridine and described in relation to the nature of the molecular orbitals that participate in the electronic transition.

**Computational Details**

Ab-initio calculations have been performed using the GAMESS program package developed by Dupuis and co-workers, employing the 6-31G basis set. Optimized geometries of pyrimidine have been calculated for the ground state and the lowest \( ^3B_1(n^*) \), \( ^3A_2(n^*) \), and \( ^3A_1(\pi^*) \) states. Two approaches have been exploited: In the first instance, the geometry of the molecule in the ground state and the triplet states has been optimized at the RHF and UHF levels of approximation, respectively. Subsequently, geometry optimizations have been performed using the CASSCF approach for the \( n \) and \( \pi \) electron molecular-orbital space. In the latter calculations, all possible configurations of the proper symmetry which arise from assigning the four \( n \) electrons and the six \( \pi \) electrons of pyrimidine to two nonbonding and six \( \pi \) molecular orbitals have been used to expand the electronic wave function. The geometry optimizations have been carried out using the energy-gradient technique.

**Results**

Our principal interest concerns the geometry changes of pyrimidine upon excitation from the ground state to the \( ^3B_1(n^*) \), \( ^3A_2(n^*) \), and \( ^3A_1(\pi^*) \) states. In order to come to a meaningful discussion of these geometry changes, we have determined the equilibrium geometry of the molecule in its electronic ground state within the same computational strategy as applied for the triplet states. In Table I, we report the RHF- and CASSCF-optimized geometries of pyrimidine in its planar ground state for which energies of \(-262.564 \pm 1 \) hartree and \(-262.653 \pm 27 \) hartrees have been calculated, respectively. These energies compare favorably with those obtained in similar calculations with slightly larger basis sets for geometries that are in minor aspects different from the experimental geometry.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>RHF</th>
<th>CASSCF</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>1.346</td>
<td>1.334</td>
<td>1.346</td>
</tr>
<tr>
<td>C–N</td>
<td>1.402</td>
<td>1.406</td>
<td>1.402</td>
</tr>
<tr>
<td>N–C</td>
<td>1.107</td>
<td>1.107</td>
<td>1.107</td>
</tr>
<tr>
<td>C–H</td>
<td>1.079</td>
<td>1.079</td>
<td>1.079</td>
</tr>
</tbody>
</table>

*The energies are given in hartrees, the bond lengths in angstroms, and the bond angles in degrees.*

### Table I. Optimized Geometries of Pyrimidine in the Ground State in Comparison with the Experimentally Determined Geometry

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>RHF</th>
<th>CASSCF</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>1.385</td>
<td>1.395</td>
<td>1.393</td>
</tr>
<tr>
<td>C–N</td>
<td>1.334</td>
<td>1.346</td>
<td>1.350</td>
</tr>
<tr>
<td>N–C</td>
<td>1.330</td>
<td>1.342</td>
<td>1.332</td>
</tr>
<tr>
<td>C–H</td>
<td>1.070</td>
<td>1.071</td>
<td>1.087</td>
</tr>
</tbody>
</table>

*The energies are given in hartrees, the bond lengths in angstroms, and the bond angles in degrees.*

### Table II. Optimized Geometries of Pyrimidine in the \( ^3B_1(n^*) \) State

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>UHF</th>
<th>CASSCF</th>
<th>CASSCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>1.390</td>
<td>1.394</td>
<td>1.394</td>
</tr>
<tr>
<td>C–N</td>
<td>1.406</td>
<td>1.402</td>
<td>1.414</td>
</tr>
<tr>
<td>N–C</td>
<td>1.107</td>
<td>1.107</td>
<td>1.107</td>
</tr>
<tr>
<td>C–H</td>
<td>1.079</td>
<td>1.079</td>
<td>1.079</td>
</tr>
</tbody>
</table>

*The energies are given in hartrees, the bond lengths in angstroms, and the bond angles in degrees.*

**Figure 2.** CASSCF-optimized geometry of pyrimidine in its ground state. Also given are the numbering of the atoms and the axis system used.
ometries demonstrate that these planar geometries of do not represent true minima on the potential energy surface of the 3A2(nπ*) state but should be considered as saddle points of the H7-C2-N1 (H7-C2-N3) bond angle. The force constant of the N1-CrN3 bond angle decreases (with a concurrent increase to a good approximation still planar. As compared to the ground-state geometry, the changes in bond lengths and bond
angles are qualitatively similar for the optimized geometries of the same energy. Likewise, the conformations with 300 will be of the same energy. We have at the UHF/RHF level, we observe basically the same changes, albeit slightly smaller. Calculation of the force constant matrix for the CASSCF C2h geometry of the 3B1(nπ*) state gives rise however to one imaginary frequency, indicative of the instability of this conformation at the CASSCF level. The coordinate associated with this imaginary frequency is an out-of-plane one of b1 symmetry which lowers the symmetry of the molecule from C3 to C1h, the reflection plane being the xz plane. The subsequent optimization of the geometry within C1h symmetry leads to a minimum corresponding to a nonplanar geometry for pyrimidine in the 3B1(nπ*) state at an energy 68 cm⁻¹ below that of the corresponding state in the C2h geometry. The structural parameters of this conformation are given in Table II, while the projection of the geometry on the xz plane is drawn in Figure 3. The main deviations from planarity concern the position of the C9 and the H9 atoms with respect to the plane defined by C6-N1-C2. The projection of the N1-C10-C2 bond on the xz plane makes an angle of about 10° with the x axis, while the analogous projection of the C9-H10 (C9-H3) bond makes an angle of about 13° with this axis. We notice that the C7-H1 bond remains nearly parallel to the C5-N1-C2 plane. The rest of the molecule is to a good approximation still planar. As compared to the ground-state geometry, the changes in bond lengths and bond angles are qualitatively similar for the optimized geometries of pyrimidine in the 3B1(nπ*) state under C2h and C1h symmetries.

The geometry optimization of pyrimidine in the 3A2(nπ*) state has been performed analogously to that for the 3B1(nπ*) state. First, the geometry of the molecule has been optimized within C2h symmetry at the UHF and CASSCF levels, leading to the geometries given in Table III. For the 3A2(nπ*) state, as compared to the ground state, especially the N1-C1 (N1-C2) bond lengths, the C9-N1-C2 (C9-N2-C2) bond angle increases, and the N1-C1-N3 bond angle decreases (with a concurrent increase of the H9-C1-N3 (H9-C2-N3) bond angle). The force constant matrices calculated for the UHF- and CASSCF-optimized geometries demonstrate that these planar geometries of C2h symmetry do not represent true minima on the potential energy surface of the 3A2(nπ*) state but should be considered as saddle points because one of the normal modes gives rise to an imaginary frequency in both calculations. The coordinate belonging to this frequency is once again an out-of-plane coordinate of b1 symmetry distorting the molecule from C2h to C1h symmetry, the xz plane remaining the plane of symmetry. The optimization of the geometry under the constraint of C1h symmetry results in the stable geometries at the UHF and CASSCF levels given in Table III. The corresponding UHF and CASSCF energies imply stabilizations with respect to the C2h conformation of 1192 and 495 cm⁻¹, respectively. A projection for the CASSCF-optimized structure on the xz plane is represented in Figure 4. Particularly significant is the position of the C7-H1 fragment with respect to the rest of the molecule. The projection of the N1-C10-C2 bond on the xz plane makes an angle with the x axis of 8° (9°) in the UHF (CASSCF) calculation, while the C7-H1 bond makes an angle of -29° (-23°) with this axis. The comparison of the bond lengths and bond angles in the two optimized geometries with those in the ground state shows similar changes, as previously observed for the C2h conformations of the 3A2(nπ*) state. The notable exception is the H7-C2-N1 (H7-C2-N3) bond angle which, as the result of the out-of-plane distortion of the C7-H1 fragment, becomes almost equal to that in the ground state.

Finally, we consider the calculations on the geometry of pyrimidine in the 3A2(ππ*) state. Since, in the present case, we are interested in the analogies with the in-plane deformations as they occur in the 3B1a state of benzene, we make use of the terminology associated with the ππ* vibration. This vibration is a degenerate vibration which can be expressed in the polar coordinates ρ and φ. In the definition used previously, the quinoidal conformations occur for ϕ = 0, 120, and 240°, while the antiquinoidal conformations occur for ϕ = 60, 180, and 300°. In pyrimidine, the conformations with ϕ = 120 and 240° are due to symmetry of the same energy. Likewise, the conformations with ϕ = 60 and 300° will be of the same energy. We have performed the geometry optimizations of pyrimidine in the 3A2(ππ*) state under the restriction of C1h symmetry with the yz plane as the plane of symmetry. On this cross section of the potential energy surface, we indeed find at the UHF level three minima and three saddle points of which the geometries are given in Table IV. The conformations that roughly can be described as corresponding to the antiquinoidal
conformations constitute at the UHF level the true minima, while the quinoidal conformations represent the saddle points in the trough. As will become clear from the following, the influence of the electron correlation on the geometry and relative energies of the various conformations in the $3\text{Al}(\pi\pi^*)$ state is much larger than for the $\pi^*\pi$ states. For this reason we will at this point not consider the geometry changes with respect to the ground state.

On the CASSCF level, the ordering in energy of the quinoidal and antiquinoidal conformations is reversed and even the mutual ordering of the three quinoidal conformations is changed. At this level, we have been able to locate four of the six conformations: the quinoidal conformations corresponding to $\varphi = 0^\circ$ and $\varphi = 120^\circ$ ($240^\circ$) and one of the antiquinoidal conformations, namely the one corresponding to $\varphi = 180^\circ$. The geometries are given in Table IV. In the $3\text{Al}(\pi\pi^*)$ state, the $\varphi = 0^\circ$ conformation is now the one of lowest energy while the conformation corresponding to $\varphi = 120^\circ$ ($240^\circ$) is found 630 cm$^{-1}$ higher in energy. The conformation corresponding to $\varphi = 180^\circ$ represents a saddle point, 1022 and 392 cm$^{-1}$ higher in energy than the minima obtained at $\varphi = 0^\circ$ and $\varphi = 120^\circ$ ($240^\circ$), respectively. As compared to the ground-state geometry, the main changes occur for the $\varphi = 0^\circ$ conformation in the bond length $C_1-N_1$ ($C_4-N_4$), which is shortened, and the $C_4-C_5$ ($C_1-C_2$) and $N_1-C_2$ ($N_4-C_5$) bond lengths, which are elongated; for the $\varphi = 120^\circ$ conformation, the bond lengths $C_4-C_5$ and $N_1-C_2$ are shortened while $C_4-N_4$, $C_1-C_2$, $N_1-C_2$, and $C_4-C_5$ are elongated, and for the $\varphi = 180^\circ$ conformation, the $C_4-N_4$ ($C_1-N_1$) bond is elongated.

### Table IV. Optimized Geometries for Pyrimidine in the $3\text{Al}(\pi\pi^*)$ State

<table>
<thead>
<tr>
<th></th>
<th>UHF ($\varphi = 0^\circ$)</th>
<th>CASSCF ($\varphi = 0^\circ$)</th>
<th>UHF ($\varphi = 180^\circ$)</th>
<th>CASSCF ($\varphi = 180^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4-C_5$</td>
<td>$1.295 (+0.039)$</td>
<td>$1.305 (+0.041)$</td>
<td>$1.386 (+0.056)$</td>
<td>$1.422 (+0.080)$</td>
</tr>
<tr>
<td>$C_1-N_1$</td>
<td>$1.295 (+0.039)$</td>
<td>$1.305 (+0.041)$</td>
<td>$1.386 (+0.056)$</td>
<td>$1.422 (+0.080)$</td>
</tr>
<tr>
<td>$C_2-H_6$</td>
<td>$1.069 (-0.001)$</td>
<td>$1.068 (-0.003)$</td>
<td>$1.073 (+0.002)$</td>
<td>$1.072 (+0.001)$</td>
</tr>
<tr>
<td>$C_2-H_{10}$</td>
<td>$1.071 (+0.001)$</td>
<td>$1.070$</td>
<td>$1.067 (-0.003)$</td>
<td>$1.066 (-0.004)$</td>
</tr>
<tr>
<td>$C_1-H_7$</td>
<td>$1.066 (-0.003)$</td>
<td>$1.057 (-0.009)$</td>
<td>$1.069 (+0.002)$</td>
<td>$1.068 (+0.002)$</td>
</tr>
<tr>
<td>$C_2-H_{10}$</td>
<td>$1.071 (+0.002)$</td>
<td>$1.071$</td>
<td>$1.072 (-0.002)$</td>
<td>$1.072 (-0.002)$</td>
</tr>
<tr>
<td>$H_7-C_5$</td>
<td>$1.348 (-0.037)$</td>
<td>$1.357 (-0.043)$</td>
<td>$1.397 (-0.063)$</td>
<td>$1.408 (-0.066)$</td>
</tr>
<tr>
<td>$H_7-C_{18}$</td>
<td>$1.496 (+0.166)$</td>
<td>$1.446 (+0.104)$</td>
<td>$1.460 (+0.100)$</td>
<td>$1.460 (+0.100)$</td>
</tr>
<tr>
<td>$C_6-N_1$</td>
<td>$1.252 (+0.133)$</td>
<td>$1.276 (+0.147)$</td>
<td>$1.284 (+0.152)$</td>
<td>$1.284 (+0.152)$</td>
</tr>
<tr>
<td>$N_1-C_2$</td>
<td>$1.199 (+2.2)$</td>
<td>$1.180 (+0.3)$</td>
<td>$1.168 (+0.9)$</td>
<td>$1.170 (-0.7)$</td>
</tr>
<tr>
<td>$H_6-C_2$</td>
<td>$1.118 (+2.2)$</td>
<td>$1.117 (+1.3)$</td>
<td>$1.145 (-2.2)$</td>
<td>$1.150 (-1.6)$</td>
</tr>
<tr>
<td>$C_4-N_4$</td>
<td>$1.189 (+2.2)$</td>
<td>$1.187 (+1.3)$</td>
<td>$1.215 (+0.2)$</td>
<td>$1.220 (-1.3)$</td>
</tr>
<tr>
<td>$C_1-H_7$</td>
<td>$1.175 (+0.2)$</td>
<td>$1.178 (+0.5)$</td>
<td>$1.198 (+0.8)$</td>
<td>$1.216 (-0.7)$</td>
</tr>
</tbody>
</table>

* Format as given in the footnote to Table II.

### Table V. Vertical and Relaxed Excitation Energies (eV) of the $1\text{B}(\pi^*\pi^*)$, $1\text{A}_1(\pi^*\pi^*)$, and $1\text{A}_2(\pi^*\pi^*)$ states

<table>
<thead>
<tr>
<th></th>
<th>Vertical</th>
<th>Relaxed</th>
<th>Vertical</th>
<th>Relaxed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2^{(a)}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2^{(b)}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2^{(c)}$</td>
<td></td>
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</tr>
<tr>
<td>$C_2^{(d)}$</td>
<td></td>
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</tr>
</tbody>
</table>

* Vertical excitation energy based on the CASSCF energies of the triplet states in the CASSCF-optimized geometry of the ground state.

Discussion

We first consider the relative ordering of the various triplet states. In Table V, we summarize the calculated vertical and relaxed excitation energies of the triplet states investigated here and compare these energies with the values obtained in the most extensive ab-initio calculations performed as yet.9 Experimental studies of the lowest triplet state of pyrimidine in the solid state and in the gas phase have established the $1\text{B}_2(\pi^*\pi^*)$ character.

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of this state. Our calculations fail to reproduce the energy ordering of the triplet states, since we find the \( 1A_1(\pi\pi^\ast) \) state lowest in energy, albeit that the calculated energy difference between the \( 1A_1(\pi\pi^\ast) \) and \( 1B_1(\pi\pi^\ast) \) states is very small. In the calculations of Palmer et al.,\(^{39}\) in which up to 30 electrons were correlated, the \( 1A_1(\pi\pi^\ast) \) and \( 1B_1(\pi\pi^\ast) \) states appear in proper order. Our failure is probably due to the fact that only 10 electrons have been correlated in the present calculations. A partial justification for this hypothesis can be found in recent calculations of the excitation energies of the \( 1B_1(\pi\pi^\ast) \) and \( 1A_1(\pi\pi^\ast) \) states of pyridine.\(^ {31}\) Here the \( 1A_1(\pi\pi^\ast) \) state has been calculated to be the lowest triplet state with an energy separation from the \( 1B_1(\pi\pi^\ast) \) state that changes from 1.24 eV when only the \( n \) and \( \pi \) electrons are correlated to 0.15 eV when the \( \sigma \) electrons are also taken into account. Consequently, it is to be expected that also in the present calculations the inclusion of more electrons and molecular orbitals in the treatment of the electron correlation may lower the energy of the \( 1B_1(\pi\pi^\ast) \) state more than that of the \( 1A_1(\pi\pi^\ast) \) state.

The geometry optimization for pyridine in the \( 3B_1(\pi\pi^\ast) \) state resulted at the UHF level in a planar conformation with \( C_2^v \) symmetry, while at the CASSCF level an out-of-plane distorted conformation with \( C_{3v} \) symmetry was obtained that is 68 cm\(^{-1} \) more stable than the CASSCF-optimized conformation with \( C_2^v \) symmetry. The difference between the results at the two levels of calculation underlines the important role of electron correlation. The magnitude of the stabilization energy should consequently be considered with caution, since it may depend largely on the amount of electron correlation taken into account and the size of the basis set. For the \( 1A_2(\pi\pi^\ast) \) state, the geometry optimization resulted at both levels in an out-of-plane distorted conformation. Electron correlation is also important for this state: at the UHF level a stabilization energy of 1192 cm\(^{-1} \) has been calculated, while at the CASSCF level this energy is reduced to 495 cm\(^{-1} \). It can be concluded that the stabilization energy corresponding to the out-of-plane distortion of the molecule in the \( 1B_1(\pi\pi^\ast) \) state is small and is certainly not as large as that in the \( 1A_1(\pi\pi^\ast) \) state.

We now compare the results of the calculations on the \( 1B_1(\pi\pi^\ast) \) state with the available experimental data. In the optical studies, it has been observed that the 0–0 transition and the transitions involving totally-symmetric vibrations are prominently present in the emission spectrum of the \( T_1 \) spin sublevel.\(^ {21, 22, 25} \) Such transitions would be forbidden if the molecule would retain \( C_2^v \) symmetry in the \( 1B_1(\pi\pi^\ast) \) state. Additionally, these transitions are not expected to be perturbed analogously to the \( 3B_1(\pi\pi^\ast) \) vibrational coordinate. In terms of vibronic coupling, the \( 1B_1(\pi\pi^\ast) \) and \( 1A_1(\pi\pi^\ast) \) transitions are found to be analogously polarized.\(^ {25} \) These observations have been taken as evidence for a distortion of the molecule in the \( 1B_1(\pi\pi^\ast) \) state along a \( b_1 \) coordinate.\(^ {25} \) This conclusion seems to be in conflict with the results of ODENDOR experiments on the \( 1B_1(\pi\pi^\ast) \) state. These studies have enabled an accurate determination of the hyperfine tensors of the nitrogen and hydrogen atoms.\(^ {26} \) The interpretation of these tensors has led to the conclusion that the molecule retains to a very good approximation its \( C_2^v \) symmetry upon excitation; i.e., the molecule is not statically distorted in the \( 1B_1(\pi\pi^\ast) \) state.

The conclusions drawn from the optical and the magnetic-resonance experiments are not as much in conflict as might at first seem; both conform to the picture arising from our calculations. According to the calculations of Palmer et al.,\(^ {39} \) the \( 1B_1(\pi\pi^\ast) \) state is vibronically coupled. The \( b_1 \) coordinate points to a \( 3B_2 \) vibronic transition and the transitions \( 2a_2(\pi\pi^\ast) \) and \( 2A_2(\pi\pi^\ast) \) do show up in the ODENDOR experiments. According to the calculations of Palmer et al.,\(^ {39} \) this state is only 0.2 eV above the \( 1B_1(\pi\pi^\ast) \) state, which makes such vibronic coupling likely from an energy point of view. This coupling is borne out from our calculations as well. In \( C_2^v \) symmetry, the CASSCF wave function is given by \( 0.90|7b_1(n\pi)\rangle + 0.40|7a_2(\pi\pi^\ast)\rangle \). For the optimized \( C_{3v} \) conformation substantial \( 1A_1(\pi\pi^\ast) \) character turns out to be mixed in since the CASSCF wave function is given by \( 0.80|7b_1(n\pi)\rangle - 2a_2(\pi\pi^\ast)\rangle + 0.40|1a_2(\pi\pi^\ast)\rangle + 2a_2(\pi\pi^\ast)\rangle + \ldots \). For the \( 1A_2(\pi\pi^\ast) \) state of pyrimidine, experimental data are not available. From a theoretical point of view, it is of interest to compare this state with the \( 1B_1(\pi\pi^\ast) \) state of pyridine. Both for the \( 1A_1(\pi\pi^\ast) \) state of pyrimidine and for the \( 1B_1(\pi\pi^\ast) \) state of pyridine, the excitation in first approximation corresponds to the promotion of an electron from a lone-pair orbital to the \( 3b_1(\pi\pi^\ast) \) orbital. Recent ESE experiments and ab-initio calculations on the \( 1B_1(\pi\pi^\ast) \) state of pyridine show that the molecule adopts a boatlike structure in which the nitrogen atom is tilted about 40° and the para-carbon atom by about 10° with respect to the plane defined by the ortho- and meta-carbon atoms. Intimately related with this geometry change is a rehybridization of the ortho-carbon atoms which become almost sp\(^2\) hybridized. The nitrogen atom retains, on the contrary, the sp\(^2\) hybridization it has in the ground state. The present calculations show qualitatively a similar behavior for the \( 1A_2(\pi\pi^\ast) \) state of pyrimidine. The molecule is unstable in the planar geometry and turns out to be out-of-plane distorted along a \( b_1 \) vibrational coordinate in both the UHF and CASSCF calculations. Whereas the stabilization energy depends on the level of calculation, the calculated optimized geometry hardly differs. This has also been observed in the previous calculations on the \( 1B_1(\pi\pi^\ast) \) state of pyridine.\(^ {5, 7} \) In addition, also for the \( 1A_2(\pi\pi^\ast) \) state of pyrimidine, the hybridization of the carbon atom next to the nitrogen (actually two nitrogens in this case) changes basically toward sp\(^1\), as can be deduced from the fact that the bond angle //\( C_1-C_2-N_1 \) becomes reduced from 125° in the ground state to 110° in the optimized geometry of the \( 1A_2(\pi\pi^\ast) \) state. A final point of interest concerns the state to which the \( 1A_1(\pi\pi^\ast) \) state is vibronically coupled. The \( b_1 \) coordinate points to a \( B_2 \) partner, most probably the \( 1B_1(\pi\pi^\ast) \) state, which, according to the calculations of Palmer et al.,\(^ {39} \) is about 0.8 eV higher in energy than the \( 1A_1(\pi\pi^\ast) \) state. A CASSCF calculation of this state, such a mixing of the \( 1A_1(\pi\pi^\ast) \) and \( 1B_1(\pi\pi^\ast) \) states is not obvious, since a comparison of the wave functions in \( C_2^v \) and \( C_{3v} \) symmetries does not reveal significant additional configurations in the \( C_{1u} \).

wave function. Apparently, the effects of the vibronic coupling are already incorporated at the orbital level. We notice the conclusion that the \( \tilde{A}_2 (\pi^*) \) state is coupled to the \( \tilde{B}_2 (\pi^*) \) state implies that the \( \tilde{A}_2 (\pi^*) \) state of pyridine and the \( \tilde{B}_2 (\pi^*) \) state of pyrimidine are subject to a vibronic coupling with basically different \( \pi^* \) states. In pyridine, the vibronic coupling takes place with the \( \pi^* \) orbital of MO parentage similar to that of the \( \tilde{B}_{1g} \) state of benzene. In pyrimidine, the vibronic coupling takes place with the \( \pi^* \) state of MO parentage similar to that of the \( \tilde{B}_{2e} \) state of benzene.

The above discussed results of the calculations on the \( \tilde{B}_2 (\pi^*) \) state and \( \tilde{A}_2 (\pi^*) \) state have shown in which aspects pyrimidine is subject to conformational changes upon excitation to either one of these \( \pi^* \) states. In a coarse interpretation, one could say that the molecule undergoes the same type of structural changes in the sense that for both states distortions to out-of-plane geometries are calculated at the CASSCF level. The finer details of these out-of-plane changes are however markedly different for the two states. Excitation to the \( \tilde{B}_2 (\pi^*) \) state brings about a relatively small out-of-plane distortion of the \( C_2H_6 \) and \( C_2H_4 \) fragments with such a small stabilization energy with respect to the \( C_2 \) geometry that explicit electron correlation is necessary for this out-of-plane distortion to show up. The excitation to the \( \tilde{A}_2 (\pi^*) \) state, on the other hand, results in a large out-of-plane distortion of the \( C_7H_7 \) fragment with a large stabilization energy, indicating that the vibronic coupling between the \( \tilde{A}_2 (\pi^*) \) and \( \tilde{B}_2 (\pi^*) \) states is considerably stronger than the vibronic coupling between the \( \tilde{B}_2 (\pi^*) \) and \( \tilde{A}_2 (\pi^*) \) states.

Apart from a description of the geometry changes occurring upon excitation to the \( \pi^* \) states in terms of vibronic coupling, it is instructive to consider these changes from the point of view of the electronic structure, as in our previous theoretical study of the \( \tilde{B}_1 (\pi^*) \) state of pyridine. We argued that an azabenzenoid in the \( \pi^* \) state can be well susceptible to out-of-plane distortions, because the \( \pi \)-electron system in this kind of molecules becomes in first approximation a 7-\( \pi \)-electron system and thus is no longer aromatic. Because it is the excited electron that reduces the stabilization energy, we speculated that the kind of distortion the molecule undergoes might be intimately connected with the nature of the \( \pi^* \) orbital involved in the excitation. Such a reasoning adequately described the observations for pyridine. The present results on the \( \pi^* \) states of pyrimidine show that the geometry changes conform to the nature of the \( \pi^* \) orbital in this case as well. For the \( \tilde{B}_2 (\pi^*) \) state, an electron is excited to the 2a2(\( \pi^* \)) orbital, which is antibonding character between the \( C_2 \) geometry that explicit electron correlation is necessary for this out-of-plane distortion to show up. The excitation to the \( \tilde{A}_2 (\pi^*) \) state, on the other hand, results in a large out-of-plane distortion of the \( C_7H_7 \) fragment with a large stabilization energy, indicating that the vibronic coupling between the \( \tilde{A}_2 (\pi^*) \) and \( \tilde{B}_2 (\pi^*) \) states is considerably stronger than the vibronic coupling between the \( \tilde{B}_2 (\pi^*) \) and \( \tilde{A}_2 (\pi^*) \) states.

The observed geometry changes in the \( \tilde{B}_2 (\pi^*) \) state of pyrimidine and the \( \tilde{B}_2 (\pi^*) \) and \( \tilde{A}_2 (\pi^*) \) states of pyrimidine consequently seem to suggest that the geometry of the molecule is modified in a way that reduces the antibonding character of the excited-state wave function. For all of these states, this is accomplished partly by bond elongation (see also ref 7) and partly by an out-of-plane distortion of the molecule. For diazabenzeno, pyrazine, the lowest triplet state basically derives from the excitation of an electron from a lone-pair orbital into the \( 3b_3 (\pi^*) \) orbital (in D\( _{2h} \) symmetry). Since the latter orbital is the analogue of the \( 3b_1 (\pi^*) \) orbital for pyridine and pyrimidine, one might expect a tendency toward elongation of the bonds between the carbon and nitrogen atoms and/or nonplanarity. Calculations by Ellenbogen et al. on the planar pyrazine molecule of \( D_{3h} \) symmetry showed a lengthening of the carbon-nitrogen bonds, in agreement with the antibonding character of this bond in the \( 3b_3 (\pi^*) \) orbital. Magnetic-resonance experiments do not support this observation and, moreover, conclusively demonstrate that pyrazine retains its \( D_{3h} \) symmetry upon excitation into the lowest triplet state on the time scale of the ODENDOR experiment. Whether this symmetry conformation corresponds to a minimum on the potential energy surface or whether it is observed as the result of a dynamic distortion cannot be concluded as yet and deserves further theoretical attention.

Our calculations on the \( \tilde{A}_1 (\pi^*) \) state of pyrimidine have shown that vibronic coupling for this state can be compared with that for the \( \tilde{B}_1 \) state of benzene. In benzene, vibronic coupling between the \( \tilde{B}_1 \) and \( \tilde{E}_1 \) states is responsible for in-plane deformations of the molecule in the \( \tilde{B}_1 \) state. A potential energy surface has been calculated with a trough corresponding to quinoidal and antiquinoidal conformations of almost equal energies. For the \( \tilde{A}_1 (\pi^*) \) state of pyrimidine, we find that the quinoidal conformations represent stable minima, while the antiquinoidal conformations are saddle points on the potential energy surface. A comparison of the energies of the three quinoidal conformations shows that the equivalence of these conformations, present in benzene because of symmetry, is lost: the conformation corresponding to \( \varphi = 0^\circ \) is the one of lowest energy, while those corresponding to \( \varphi = 120^\circ \) and \( 240^\circ \) are found 630 cm\(^{-1}\) higher in energy. Additionally it is seen in Table IV that the description as quinoidal and antiquinoidal is an approximation. In the true symmetry coordinate \( S_3 (\rho, \varphi) \) of benzene, the changes in lengths of the bonds that are elongated in the quinoidal form are twice as small as the changes in the bond lengths that are shortened. The recent geometry optimizations of benzene in the \( \tilde{B}_1 \) state of Osamura\(^{16}\) show that the actual deformation is pretty well described by \( S_3 (\rho, \varphi) \). This is not the case for the \( \tilde{A}_1 (\pi^*) \) state of pyrimidine. For \( \varphi = 0^\circ \), the short bonds are only shortened by 0.04 \( \AA \) while the long ones are elongated by 0.08 \( \AA \). Similarly, the \( \varphi = 120^\circ \) (240\(^\circ\)) conformation shows such an asymmetry with shortenings of 0.03 and 0.04 \( \AA \) and elongations of 0.13, 0.10, and 0.07 \( \AA \). The same deviations from the \( S_3 (\rho, \varphi) \) coordinate are present in the antiquinoidal conformation with \( \varphi = 180^\circ \). Here it is unusual only the \( C_1' (\rho, \varphi) \) bond that becomes elongated upon excitation. With respect to the bond angles, we notice that none of the conformations given in Table IV exhibit significant differences as compared to the ground-state geometry. This conforms to the character of the \( S_3 \) coordinate, which merely involves changes in bond lengths. The observed conformational behavior of pyrimidine in the \( \tilde{A}_1 (\pi^*) \) state agrees qualitatively well with the idea that the original vibronic coupling between the \( \tilde{B}_2 \) and \( \tilde{E}_1 \) states in benzene still persists in pyrimidine, although the quantitative description is to a large extent affected by the introduction of the two nitrogen atoms in the aromatic system.

Conclusions

We have investigated the geometry changes in pyrimidine upon excitation to the \( \tilde{B}_2 (\pi^*) \), \( \tilde{A}_2 (\pi^*) \), and \( \tilde{A}_1 (\pi^*) \) states by ab-initio calculations at the UHF and the CASSCF levels. Each of these states is found to be subject to a strong vibronic coupling. For the \( \tilde{B}_2 (\pi^*) \) state, the conformation of minimum energy corresponds to a nonplanar molecule although the energy difference with the planar geometry is calculated to be only 68 cm\(^{-1}\). From this we deduce a dynamic out-of-plane distortion of pyrimidine in the lowest triplet state which describes consistently the results of optical as well as magnetic-resonance experiments. Excellent agreement has been found between the characteristic in-plane geometry changes predicted by our calculations and observed in the ODENDOR experiments.

The vibronic coupling between the \( ^3A_2(n\pi^*) \) and \( ^3B_2(\pi\pi^*) \) states demonstrates, in contrast, a much larger influence on the out-of-plane susceptibility of the molecule. The energy minimum for the \( ^3A_2(n\pi^*) \) state corresponds to an out-of-plane conformation which is stabilized with respect to the planar conformation by about 500 cm\(^{-1}\) in the CASSCF calculation and by about 1200 cm\(^{-1}\) in the UHF calculation.

The \( ^3A_2(\pi\pi^*) \) state has been shown to be subject to a vibronic coupling which is qualitatively similar to that between the \( ^3B_{1u} \) and the \( ^3E_{1u} \) states of benzene. The effect of introducing two nitrogen atoms in the aromatic ring manifests itself most clearly in the stabilization of the quinoidal conformation corresponding to \( \varphi = 0^\circ \); the other two quinoidal conformations are 630 cm\(^{-1}\) higher in energy, while the anti-quinoidal conformations form the saddle points in the trough.

Finally, we have considered the description of the geometry changes in the \( n\pi^* \) states in relation to the nature of the \( \pi^* \) orbital to which a lone-pair electron is in first approximation excited. Taking into account as well previous results on the \( ^3B_{1u}(n\pi^*) \) state of pyridine, it has been shown that the structural response of the molecule to an \( n\pi^* \) excitation correlates remarkably well with the nodal-plane structure of the \( \pi^* \) orbital. This structural response shows up partly in the elongation of bonds and partly in out-of-plane distortions. Though an \( n\pi^* \) state in azabenzynes by its intrinsic nature seems to be susceptible to out-of-plane deformations, the contribution of such out-of-plane distortions to the total geometry relaxation does not have to dominate the structural response to the excitation.

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Clusters of Phosphorus: A Theoretical Investigation

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Abstract: A variety of phosphorus clusters up to \( \text{P}_{16} \) has been studied with ab initio SCF and MP2 calculations. Many of the larger clusters are found to be energetically stable with respect to \( \text{P}_4 \). The more interesting clusters are characterized by their equilibrium structures and NMR chemical shieldings and partially characterized by vibrational spectra to facilitate detection of the molecules. A probable reaction scheme for the formation of red phosphorus from white phosphorus emerges, and possible structural units of red phosphorus are established.

I. Introduction

"Precise molecular structure data for the various forms (of phosphorus) is still limited and although their inter-conversion can, in most cases, be carried out, many of the phenomena involved remain imperfectly understood." Some of these gaps can now be filled with results from large-scale ab initio calculations. Previous attempts were directed toward small clusters up to \( \text{P}_4 \), which were suspected to be present in the vapor phase along with \( \text{P}_2 \) and \( \text{P}_3 \). A notable theoretical contribution came from Jones and Hohl\(^1\) who systematically explored clusters up to \( \text{P}_{16} \) with a simulated annealing technique based on the density functional method. Their most striking results are the prediction of a "cuneane" \( \text{P}_8 \) molecule as the most stable cluster besides tetrahedral \( \text{P}_4 \) and the prediction of a moderately stable \( \text{P}_6 \) cluster with \( \text{P}_2 \) and \( \text{P}_4 \). A notable theoretical contribution came from Jones and Hohl\(^1\) who systematically explored clusters up to \( \text{P}_{16} \) with a simulated annealing technique based on the density functional method. Their most striking results are the prediction of a "cuneane" \( \text{P}_8 \) molecule as the most stable cluster besides tetrahedral \( \text{P}_4 \) and the prediction of a moderately stable \( \text{P}_6 \) cluster with \( \text{P}_2 \) and \( \text{P}_4 \).

In this work we focus attention on even-membered larger phosphorus clusters up to \( \text{P}_{32} \). Odd-membered clusters were not investigated, since our aim was to find phosphorus clusters and chain polymers which are energetically more stable than \( \text{P}_4 \), and radicals are unlikely candidates. Three major types of clusters will be considered: isolated polyhedral clusters, \( \text{P}_n \) units linked by single bonds, and polyhedral units linked by two single bonds. From these investigations a consistent scheme of formation and structural features of red phosphorus emerges, which has some bearing on violet (Hittorf) phosphorus.\(^\text{4}\) We further obtain hints for the possible existence of \( \text{P}_{12} \) and \( \text{P}_{16} \) clusters as new forms of phosphorus.

In our choice of potentially favorable structures we have been guided by chemical intuition and by a wealth of structures of substituted phosphines\(^3\) and polyphosphides.\(^\text{6}\) However, some of those structural units do not lend themselves to medium-sized clusters. This includes the odd-membered subunits \( \text{P}_3 \) and \( \text{P}_5 \) which can only occur in larger aggregates unless dangling bonds are saturated.

II. Details of Computation

SCF and MP2 treatments as well as SCF force field calculations to compute vibrational frequencies have been carried out with the program system TURBOMOLE.\(^\text{3}\) NMR shielding constants were computed by the SCF/GIAO method\(^\text{6}\) with the program SHEILA,\(^\text{7}\) which uses a semidirect algorithm for the solution of coupled-perturbed Hartree-Fock (CPHF) equations for the magnetic field as perturbation.

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