methyl groups at C-6 in II and IV at low temperatures are much greater than those between the two methyl groups at C-2 in III and IV, in agreement with the presence of an approximate *local* C_2 axis passing through C-2 in the preferred boat–chair conformations of these compounds. Methyl groups at C-6, by contrast, are in very different environments, the axial methyl group having gauche γ shielding interactions[15] with the methylene groups at positions 4 and 8 in the boat–chair, whereas the equatorial methyl group lacks any γ interaction.

The chemical shifts of C-4 and C-8 in III are at higher field than in I as a result of gauche γ shielding effects[15] of the geminal methyl groups in III. Since one methyl group shields C-4 while the other shields C-8, the shielding effects should be similar, as observed, viz., 5.6 and 6.2 ppm. The resonances of C-5, C-6, and C-7 in III should not be strongly influenced by the methyl groups, and indeed the chemical shifts of these nuclei are similar to those found in I. The α and β effects resulting from the introduction of geminal methyl groups in I to give II, III, and IV are fairly large and deshielding, as expected.[15]

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(7) This expression is strictly valid for an exchange process between two equally populated sites and where exchange is the only broadening effect; errors resulting from coupling and natural line-width effects are least when the chemical shift difference is greatest. The experimental data available are not suitable for obtaining meaningful values of $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$, even through the errors in $\Delta G^{\ddagger}$ are not large [F. A. L. Anet and R. Anet, "Dynamic Nuclear Magnetic Resonance Spectroscopy", F. A. Cotton and L. M. Jackman, Ed., Academic Press, New York, N.Y., 1975, p 543].

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(10) F. A. L. Anet, J. Krane, and I. Yavari, unpublished work. We have not carried out strain-energy calculations on 1,3-dioxocane itself because of the difficulty of taking into account the dipole–dipole energy of the cyclic acetal system.

(11) It may seem paradoxical that the twist-boat-chair, which has C_2 symmetry in cyclooctane, gives rise to a time-averaged C_s symmetry when that conformation is an intermediate in the pseudorotation of the BC-1,3 form of 1,3-dioxocane (I). The TBC conformation in cyclooctane has only a C_2 axis, and this axis bisects *bonds* on opposite sides of the molecule, whereas I, because of its substitution pattern, can only have a C_2 axis passing through opposite ring *atoms*. Thus all twist-boat-chairs of I are unsymmetrical. The C_s time-averaged symmetry must occur if either the BC-1,8 or the BC-4,6 conformations are intermediates, although it is not necessary that any intermediate have C_s symmetry for a C_s time-averaged symmetry to occur.

(12) Ring inversion can be (strictly) defined as a process that results in all the ring torsional angles changing their signs but without any change in their absolute magnitudes.[1] We shall use a generalized definition in which small changes in the magnitudes of ring torsional angles are allowed, and where time-averaged torsional angles can be used when another process is much faster than ring inversion.[1]

(13) The overall change described in Scheme II is a ring inversion only if an appropriate second process (e.g., pseudorotation via the twist-boat-chair) is already fast.[12]

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The Electronic Structure of Molecules by a Many-Body Approach. IV. Ionization Potentials and One-Electron Properties of Pyrrole and Phosphole

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Abstract: The valence ionization potentials (IP's) of pyrrole and (the presently still unknown) phosphole molecule are studied by an ab initio many-body approach which includes the effect of electron correlation and reorganization beyond the Hartree–Fock approximation. Whereas for pyrrole the first IP is due to the $1a_2(\pi)$ molecular orbital, the first IP of phosphole is due to the $2b_1(\pi)$ orbital. For the valence IP's at higher energy there is also little agreement in the ordering. For pyrrole the Hartree–Fock approximation appears to supply the correct ordering, but it does not give the correct ordering in the case of phosphole. For pyrrole there are two IP's due to σ-type orbitals between the IP's due to the π orbitals and for phosphole none. A number of one-electron properties are calculated in the one-particle approximation and compared with available experimental and theoretical data. The localized molecular orbitals are discussed as well.

I. Introduction

The five-membered heterocyclic molecules furan, thiophene, pyrrole, and phosphole have very similar structures and are isoelectronic in the valence electrons. A great similarity in the photoelectron spectra (PES) is thus expected and can be found when the gross features of the PES of these molecules are examined.[2,3] Starting with the low binding energy region the spectra consist of two well-resolved bands which correspond to the IP's due to the first two π orbitals and which frequently exhibit vibrational structure. A more detailed look at the assignment of the various peaks reveals, however, considerable differences among the molecules in particular concerning the position of the third π orbital.

Only a small number of experimental investigations of

Table I. Different Experimental and Theoretical Assignments Proposed for the Photoelectron Spectrum of Pyrrole

Derrick et al.[3]	$1a_2(\pi)$	$2b_1(\pi)$	$6a_1$	$1b_1(\pi)$	$4b_2$	$5a_1$	$3b_2$	$4a_1$	$2b_2$	$3a_1$
CNDO/2[8]	$1a_2(\pi)$	$2b_1(\pi)$	$6a_1$	$4b_2$	$5a_1$	$3b_2$	$1b_1(\pi)$	$4a_1$	$2b_2$	$3a_1$
CNDO/2[10]	$1a_2(\pi)$	$2b_1(\pi)$	$4b_2$	$6a_1$	$3b_2$	$5a_1$	$1b_1(\pi)$	$2b_2$	$4a_1$	$3a_1$
INDO[10]	$1a_2(\pi)$	$2b_1(\pi)$	$4b_2$	$6a_1$	$3b_2$	$5a_1$	$1b_1(\pi)$	$2b_2$	$4a_1$	$3a_1$
INDO[9]	$1a_2(\pi)$	$2b_1(\pi)$	$4b_2$	$6a_1$	$1b_1(\pi)$	$5a_1$	$3b_2$	$4a_1$	$2b_2$	$3a_1$
EH[10]	$1a_2(\pi)$	$2b_1(\pi)$	$6a_1$	$4b_2$	$5a_1$	$3b_2$	$1b_1(\pi)$	$4a_1$	$2b_2$	$3a_1$
ARCANA[10]	$1a_2(\pi)$	$2b_1(\pi)$	$6a_1$	$4b_2$	$5a_1$	$3b_2$	$1b_1(\pi)$	$4a_1$	$2b_2$	$3a_1$
Genson et al.[15]	$1a_2(\pi)$	$2b_1(\pi)$	$6a_1$	$1b_1(\pi)$	$4b_2$	$3b_2$	$5a_1$	$4a_1$	$2b_2$	$3a_1$
Pullman et al.[13]	$1a_2(\pi)$	$2b_1(\pi)$	$6a_1$	$4b_2$	$1b_1(\pi)$	$3b_2$	$5a_1$	$4a_1$	$2b_2$	$3a_1$
Clementi et al.[12] and Palmer et al.[14]	$1a_2(\pi)$	$2b_1(\pi)$	$6a_1$	$4b_2$	$3b_2$	$1b_1(\pi)$	$5a_1$	$4a_1$	$2b_2$	$3a_1$
Preston et al.[16]	$1a_2(\pi)$	$2b_1(\pi)$	$6a_1$	$4b_2$	$1b_1(\pi)$	$3b_2$	$5a_1$	$4a_1$	$2b_2$	$3a_1$
This work	$1a_2(\pi)$	$2b_1(\pi)$	$6a_1$	$4b_2$	$1b_1(\pi)$	$3b_2$	$5a_1$	$4a_1$	$2b_2$	$3a_1$

the PES of pyrrole exists,[3-6] but there are a fairly large number of theoretical calculations.[5,7-16] Derrick et al.[3] and Gelius et al.[6] made an assignment of the PES of pyrrole. Derrick et al. used photoelectron spectroscopy (He(I) and He(II) line), Rydberg series, mass spectrometry, an extended Hückel calculation, and a comparsion with furan and pyridine for the assignment, whereas Gelius et al. based their work on the ESCA spectrum, the assignment of Derrick et al., computed intensities, and the ab initio calculation of Clementi,[12] but we were not able to decide between the assignment by Derrick et al. and the results of Clementi. The various theoretical calculations, both the semiempirical[8-10] and the ab initio ones,[11-16] are at considerable variance with each other. In Table I we have compiled the different experimental and theoretical assignments of the PES of pyrrole. There is agreement concerning the first two IP's which are due to the $1a_2(\pi)$ and the $2b_1(\pi)$ molecular orbitals (MO's), but the calculations already do not agree on the assignment of the third IP which is assumed to be due to either an a_1- or a b_2-type MO. The semiempirical methods place four orbitals of σ-type symmetry between the $1b_1(\pi)$ and the $2b_1(\pi)$ MO's except for the modified INDO method of Ridley and Zerner.[9] The ab initio calculations place one,[15] two,[13,16] or three[12] MO's of σ-type symmetry between these two π orbitals. Among these the calculation of Preston and Kaufman[16] is definitely the most reliable one. The other calculations employ minimal basis sets[12,14] or even smaller ones.[13,15] In view of the importance of the pyrrole molecule and the understanding of its electronic structure it appears necessary to perform a more accurate calculation on the IP's which goes beyond the Hartree-Fock (HF) approximation and includes the effect of electron correlation and reorganization on the IP's. This has been done in the present study for all IP's below about 21 eV (energy of the He(I) line). The same has been done for the homologous but still unknown phosphole molecule. Section II contains a short description of the method. The wave functions and the results for the IP's are discussed in section III. In section IV a number of one-electron properties which are calculated in the one-particle approximation are presented and compared to experimental and other theoretical work. The localized molecular orbitals are discussed as well.

II. Method of Calculation

In the present many-body approach the IP's including the effects of electron correlation and reorganization are calculated directly. Only the wave function of the electronic ground state in the HF approximation is required for this purpose. To obtain the corrected IP's, ω, the Dyson equation[17] is solved, i.e., one looks for those values ω for which the eigenvalues of $\epsilon + \Sigma(\omega)$ are equal to ω. ϵ is the diagonal matrix of orbital energies resulting from the SCF calculation on the electronic ground state; Σ is called self-energy and is essentially the exact potential seen by an electron due to the interactions with and in its surroundings except for the HF potential whose effect is incorporated into the orbital energies. The self-energy is expanded in a perturbation series where all terms up to and including the third order are taken into account exactly and higher order terms are approximated by a renormalization procedure. Since the first-order term in this expansion is zero if one starts with canonical HF orbitals the first-order solution of the Dyson equation yields Koopmans' theorem.[18] The second and higher order solutions contain the effect of electron correlation and reorganization to greater and greater accuracy. The details of the method have been presented in ref 19 and 20 where the relation to other methods is discussed as well. Only the most closely related methods will be mentioned. Pickup and Goscinski[52] have proposed an operator method to evaluate the self-energy. Some approximations in this scheme have been used by Purvis and Öhrn[53] to calculate IP's. Yarlagadda et al.[54] employed a functional differentiation technique to calculate Σ for He. Simons and Smith[55] used an equation of motion method, whereas Chong et al.[56] and Hubač et al.[57] have applied time-independent perturbation techniques to the problem of calculating IP's. The present many-body approach has been successfully applied to a number of molecules.[21-31] Some assignment problems in the PES of cyanogen,[26] formaldehyde,[27] sulfur hexafluoride,[28] benzene,[29] and heterocyclic molecules[30,31] could thereby be resolved.

The eigenvectors of the matrix $\omega \mathbf{1} - \epsilon - \Sigma$ are, in all cases examined, very close to unit vectors. This justifies a diagonal approximation to the Dyson equation, which has been done for the third order and renormalized results. In addition this fact supplies the valuable information that the orbital picture for describing the electronic structure of molecules is a good approximation. Ionization can thus in general be regarded as a physical process occurring essentially from a single orbital even in the case where correlation and reorganization are taken into account. This by itself is an important result which may be difficult to obtain otherwise.

The present approach differs markedly from the standard method of calculating accurate IP's. By standard method it is meant that the IP's are calculated as differences of total energies as obtained from wave functions including configuration interaction for the ground as well as the ionic states. The advantages of the many-body approach are that only the wave function for the electronic ground state is required. Correlation and reorganization are taken into account on an equal footing for both states, the neutral and the ionic one, which may be difficult to achieve with the standard method, and the IP's are not calculated by subtracting the large absolute energies to obtain the small-energy difference.

Table II. Assumed Geometrical Parameters for Phosphole[a]

C_1-C_2	1.45 Å	∠CPC	92°
C_1-C_3	1.36 Å	∠C_2C_4P	111.5°
C_3-P	1.73 Å	∠$C_1C_2C_4$	112.5°
C-H	1.08 Å	∠PC_4H_4	119.5°
P-H	1.45 Å	∠$C_1C_2H_2$	123.5°

[a] It was pointed out by a referee that the CPC angle was chosen too acute and that a value of 102° would be preferable. The angle of 92° could cause the H atom bonded to the P atom to prefer a position outside the plane of the ring.

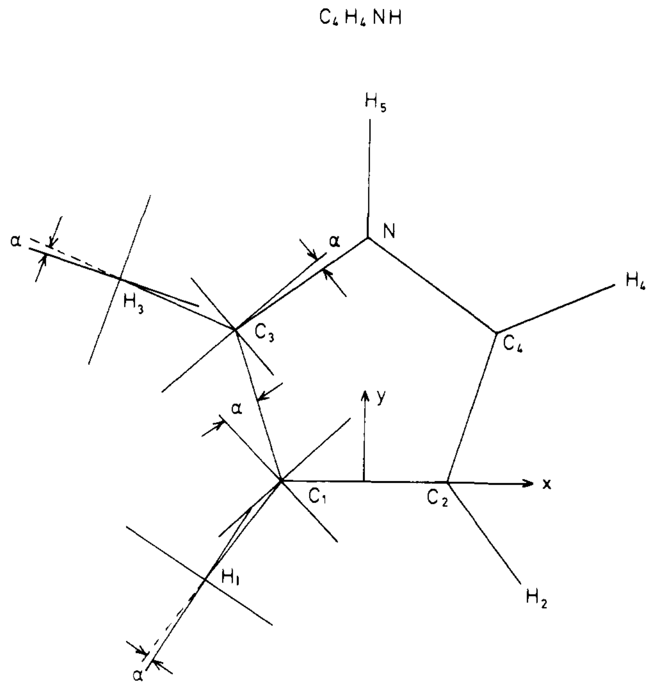

Figure 1. Coordinate system, numbering of atoms, and definition of rotation angles for the electric field gradients for pyrrole.

III. Results and Discussion of the IP's

For the calculation on the pyrrole molecule the geometry of Bak et al.[32] has been used. For the phosphole molecule the geometry has been guessed and the geometrical parameters are given in Table II. The calculated IP's and molecular properties are thus hypothetical, and may depart from the correct values should the real geometry of the molecule differ from the guessed one. The coordinate system and the numbering system of the atoms is given in Figure 1 for pyrrole and is the same for phosphole. The calculations have been performed using Roothaan's finite expansion method[33] as implemented in the program system MUNICH.[34] The basis set consists of Cartesian Gaussian functions and is of double ζ quality: (12s 9p 1d/9s 5p/4s)/[6s 4p 1d/4s 2p/2s]. The exponential parameters and contraction coefficients have been taken for the P atom from the work of Veillard[35] and for the C, N, and H atoms from the work of Huzinaga.[36] The exponential parameter of the d-type function on the P atom was taken to be $\alpha = 0.45$. The importance of this function is very small and it has only been added to improve the quantitative description in the many-body calculation. The total energies and orbital energies are listed in Table III. The total energies are compared with other theoretical results available in the literature. The lowest total energy has been calculated for pyrrole by Preston and Kaufman[16] whose basis set is very similar to the present one, but who contracted the s-type functions on the H atoms less and added a set of p-type polarization functions on all H atoms. The ordering of the orbitals is the same as in the present SCF calculation. The orbitals have been numbered starting with the first valence orbital since we are not interested in the core orbitals.

Table III. Total Energy and Orbital Energies (in eV) for the Pyrrole and Phosphole Ground State[a]

C_4H_4NH		C_4H_4PH	
Orbital	ε	Orbital	ε
a_1	−424.95	a_1	−2176.52
		b_2	−306.27
b_2	−306.84	a_1	−306.27
a_1	−306.84	a_1	−306.02
		b_2	−306.00
a_1	−305.62	a_1	−202.84
b_2	−305.59	a_1	−147.59
		b_2	−147.58
		$b_1(\pi)$	−147.55
$1a_1$	−34.95	$1a_1$	−30.87
$2a_1$	−28.30	$1b_2$	−26.38
$1b_2$	−26.65	$2a_1$	−24.73
$3a_1$	−21.38	$3a_1$	−20.10
$2b_2$	−20.84	$2b_2$	−19.77
$4a_1$	−20.08	$4a_1$	−18.86
$5a_1$	−16.22	$5a_1$	−15.56
$3b_2$	−15.83	$3b_2$	−15.47
$1b_1(\pi)$	−15.44	$6a_1$	−14.10
$4b_2$	−15.01	$1b_1(\pi)$	−13.45
$6a_1$	−14.44	$4b_2$	−13.18
$2b_1(\pi)$	−9.54	$1a_2(\pi)$	−8.75
$1a_2(\pi)$	−8.31	$2b_1(\pi)$	−7.89
Virtual Orbitals			
$7a_1$	4.58	$3b_1(\pi)$	3.41
$3b_1(\pi)$	4.60	$7a_1$	3.44
$2a_2(\pi)$	6.15	$5b_2$	3.87
$8a_1$	6.40	$2a_2(\pi)$	5.65
$5b_2$	6.53	$8a_1$	5.81
$9a_1$	6.91	$9a_1$	6.30
$6b_2$	7.16	$6b_2$	6.76
$7b_2$	9.28	$10a_1$	7.50
$10a_1$	9.52	$7b_2$	7.56
$8b_2$	10.09	$4b_1(\pi)$	8.92
$E_{tot}^{SCF} = -208.693\,968\,0$ au ($-208.776\,441\,5$ au[16]) ($-207.931\,35$ au[12]) ($-208.157\,34$ au[14]) ($-178.364\,67$ au[15])		$E_{tot}^{SCF} = -494.811\,946\,4$ au	

[a] The orbitals are numbered consecutively starting with the first valence orbital because our main interest is in the valence IP's. This numbering also facilitates a comparison between the valence isoelectronic molecules.

The ordering of the orbitals is markedly different for the two molecules. The first two MO's from the ionization limit are π orbitals, but whereas for pyrrole the first MO is of a_2 symmetry, it is of b_1 symmetry in the case of phosphole. The a_2 MO has a node through the heteroatom. A similar reversal in the orbital sequence has been found in going from pyridine to phosphoridine. In the case of these two molecules the explanation was proposed that the electron-withdrawing N atom stabilizes the b_1 component of the e_{1g} orbital in benzene, and the electron-releasing P atom stabilizes the a_2 component.[30] In the present case the N atom is electron withdrawing and the P atom remains essentially neutral as found by the population analysis to be discussed below. But in the heterocyclic five-membered molecules this feature cannot be used to explain the reversal in the MO sequence since in the system furan-thiophene no reversal is found and the charge-withdrawing or -releasing property of the heteroatom is nearly the same as in the case of pyrrole

Table IV. Mulliken Population Analysis for Pyrrole and Phosphole

Atom	C_4H_4NH	C_4H_4PH
	Gross Atomic Populations	
C_1	6.215	6.179
C_3	6.082	6.246
H_1	0.814	0.817
H_3	0.823	0.810
N, P	7.420	15.059
H_5	0.712	0.838
	Overlap Populations	
C_1-C_2	1.121	1.139
C_1-C_3	1.318	1.295
C_1-H_1	0.626	0.639
C_3-H_3	0.659	0.638
C_3-N(P)	0.802	0.949
N(P)-H_5	0.663	0.673
C_1-H_2	−0.051	−0.054
C_1-C_4	−0.034	−0.041
C_1-H_3	−0.012	0.001
C_1-N	−0.212	−0.206
C_3-H_1	−0.081	−0.085
C_3-H_5	−0.028	−0.022
C_3-C_4	−0.298	−0.297
N(P)-H_3	−0.087	−0.114

and phosphole. An explanation might emerge if one considers only the π populations of the heteroatoms.[58] The total π populations are 1.67 (N), 3.65 (P), 1.77 (O), and 3.75 (S). Taking into account the inner-shell π orbital on the P and the S atom it is seen that the populations are so similar that no explanation can be deduced. In the absence of any reasonable explanation the reversal must be taken as a property of the P atom in conjugated heterocyclic systems. The third MO is of a_1 symmetry in pyrrole and b_2 symmetry in phosphole. The third π orbital which is essentially a lone-pair orbital on the heteroatom is separated in pyrrole by two σ-type MO's from the second π orbital and in phosphole by only one. There is a considerable difference also in the ordering of the remaining valence orbitals and in the ordering of the virtual orbitals. All occupied valence orbitals in pyrrole have higher IP's than the orbitals in phosphole which can be explained by the larger electronegativity of the N atom compared to the P atom which leads to a stronger binding of the electrons in pyrrole.

The chemical shift of the inner-shell energies of the structurally different C atoms has been discussed by Gelius et al.[6] The experimental splitting for pyrrole is 0.98 eV from the ESCA spectrum and 1.2 eV from the present calculation. For phosphole the splitting is calculated to be 0.26 eV.

The results of the Mulliken population analysis[37] are listed in Table IV. The gross atomic charges indicate that the N atom gains approximately 0.4 electron which is withdrawn from the neighboring C atoms and the H atom bonded to the N atom. The P atom remains essentially neutral. The situation is the same as has been found in the case of furan and thiophene. The structure of the overlap populations is very similar for both molecules and is the same as found for furan and thiophene. The C_1C_3 overlap population is larger than the C_1C_2 overlap population in agreement with the fact that the C_1-C_3 bond length is shorter than the C_1-C_2 bond length. The C_3P overlap population is larger than the C_3N value which is again similar to the situation found for furan and thiophene. If thiophene is regarded as more aromatic than furan then phosphole might be regarded as more aromatic than pyrrole, but any such conclusions based on a population analysis must be regarded with extreme caution. The data of the population analysis agree with the values obtained by Preston and Kaufman[16] except for the C_1C_4 overlap population which is significantly more negative in their work. Since our results are consistent with the data for furan and thiophene[31] the difference might be due to the basis set dependence of the populations.

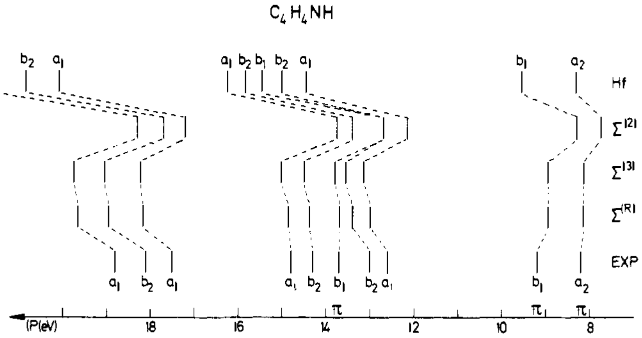

Figure 2. Experimental and calculated vertical ionization potentials of pyrrole.

The convergence of the corrected IP's with enlargement of the orbital basis set has not been examined in the present case; only the experience from the previous examinations has been used.[28-31] All occupied valence orbitals have been included in the calculations since the core orbitals hardly contribute to the corrections. For pyrrole (phosphole) 30 (31) virtual orbitals have been taken into account in the second-order calculation and 16 (15) in the third-order calculation except for some critical IP's for which 19 or 23 virtual orbitals have been taken into account. It has been found in previous work that the dominant contributions to the corrections are already obtained with a very small set of virtual orbitals. The small shifts obtained by enlarging the basis set of virtual orbitals soon become insignificant compared to the errors contained in the orbital energies themselves due to the use of a basis of Gaussian functions which gives results far from the HF limit.

The final results for the valence IP's of pyrrole which lie in the energy range of the He(I) line are listed in Table V and are graphically presented in Figure 2. The following data are given: IP's in the HF approximation, in second and third order of the perturbation expansion ($\Sigma^{(2)}$, $\Sigma^{(3)}$) the renormalized final results ($\Sigma^{(R)}$), and the experimental vertical IP's of Derrick et al.[3] (they are derived from band maxima not from band centroids with which our results should be compared[38,39]) which in their majority are considerably uncertain. In addition the pole strengths, P_i, are listed. They also have a physical meaning which is discussed in the following. Without taking correlation effects into account the self-energy vanishes and the IP's are then equal to $-\epsilon_i$, i.e., ionization processes which correspond to ejection of one electron and a simultaneous excitation of other electrons to unoccupied orbitals cannot take place. If many-body effects are taken into account, the Dyson equation has additional solutions which correspond to these processes. The pole strengths, P, in the one-particle approximation are equal to unity for the simple ionization process and zero otherwise. When many-body effects are included, the P_i are less than unity for the simple ionization process and $1 - P_i$ gives the probability for satellite lines due to excitations accompanying photoionization. For more details see ref 51. For pyrrole all pole strengths are between 0.82 and 0.93 and for phosphole (Table VI) between 0.83 and 0.93 except for the $3a_1$ IP in phosphole which has a pole strength of 0.56, i.e., one may expect satellite lines in the PES with about 7 to 18% of the intensity of the principal valence lines except for the $3a_1$ IP of phosphole which is expected to have relatively strong satellite lines.

Table V. Final Results for the Valence IP's of Pyrrole

MO	IP(HF)	IP($\Sigma^{(2)}$)	$P^{(2)}$	IP($\Sigma^{(3)}$)	$P^{(3)}$	IP($\Sigma^{(R)}$)	$P^{(R)}$	IP(exptl)[a]	Δ = IP($\Sigma^{(R)}$) − IP(exptl)
$1a_2(\pi)$	8.31	7.75	0.91	8.14	0.92	8.17	0.92	8.21	−0.04
$2b_1(\pi)$	9.54	8.31	0.90	8.94	0.92	8.92	0.92	9.20	−0.28
$6a_1$	14.44	12.15	0.89	13.14	0.93	12.98	0.92	12.60	0.38
$4b_2$	15.01	12.69	0.84	13.56[b]	0.82[b]	13.39[b]	0.82[b]	~13.0	~0.39
$1b_1(\pi)$	15.44	12.70	0.90	13.78[b]	0.93[b]	13.70[b]	0.93[b]	~13.7	~0
$3b_2$	15.83	13.41	0.89	14.51	0.92	14.37	0.92	~14.3	~0.07
$5a_1$	16.22	13.74	0.89	15.02	0.93	14.86	0.92	~14.8	~0.06
$4a_1$	20.08	17.21	0.85	18.23	0.85	18.17	0.85	~17.5	~0.67
$2b_2$	20.86	17.69	0.85	19.05	0.86	18.96	0.86	~18.1	~0.86
$3a_1$	21.38	18.30	0.85	19.75	0.87	19.64	0.87	~18.8	~0.84

[a] Reference 3. [b] Calculated with a basis set of 23 virtual orbitals.

Table VI. Final Results for the Valence IP's of Phosphole

MO	IP(HF)	IP($\Sigma^{(2)}$)	$P^{(2)}$	IP($\Sigma^{(3)}$)	$P^{(3)}$	IP($\Sigma^{(R)}$)	$P^{(R)}$
$2b_1(\pi)$	7.89	7.44	0.91	7.57	0.93	7.50	0.93
$1a_2(\pi)$	8.75	7.79	0.89	8.26	0.92	8.14	0.92
$1b_1(\pi)$	13.45	11.37	0.84	12.07[a]	0.82[a]	11.92[a]	0.82[a]
$4b_2$	13.18	11.24	0.89	12.27[a]	0.93[a]	12.06[a]	0.92[a]
$6a_1$	14.10	11.70	0.88	13.04	0.92	12.87	0.92
$3b_2$	15.47	12.77	0.88	14.27	0.91	14.11	0.91
$5a_1$	15.56	13.25	0.88	14.38	0.92	14.23	0.91
$4a_1$	18.86	16.03	0.85	17.31	0.83	17.17	0.84
$3a_1$	20.10	17.14	0.81	17.81	0.51	17.79	0.56
$2b_2$	19.77	16.77	0.85	18.14	0.83	18.01	0.83

[a] Calculated with a basis set of 19 virtual orbitals.

The IP's in the HF approximation agree well with the experimental values for the first two orbitals of pyrrole, the $1a_2$ and $2b_1$ π orbitals. All other IP's are calculated too high by one to two electron volts. Shifts of this magnitude are thus required to obtain agreement with the experimental values. In the second-order calculation large shifts are obtained and the IP's are now calculated too low. In addition the $1b_1(\pi)$ and the $4b_2$ orbitals are estimated to have nearly the same IP. The third-order calculation shifts the IP's back to higher binding energies and the $1b_1(\pi)$ IP is now back at higher binding energy than the $4b_2$ IP by 0.31 eV. The renormalization introduces only very small further shifts and changes nothing in the ordering of the orbitals. Based on these calculations the $1b_1$ IP is larger than the $4b_2$ IP but they are so close in energy that their relative order cannot unambiguously be established, especially since the difference in shifts from the HF values is about 0.3 eV. This present ordering is not in agreement with the assignment by Derrick et al.[3] but it agrees with the theoretical calculation by Preston and Kaufmann.[16] The present assignment disagrees with the assignment by Derrick et al. also in the order of the $3b_2$ and $5a_1$ IP's.

The agreement of the calculated and experimentally determined IP's is very satisfactory for the majority of the cases as can be seen from the last column of Table V. The main cause for the differences is the error in the orbital energies themselves due to the limited basis set which gives results far from the HF limit. The renormalization method used in the present work is particularly suited to describe higher order many-body effects for the outer valence orbitals.[20] This explains the better agreement found with experiment for these orbitals. It must be noted also that the experimental values are considerably uncertain and are given as approximate values by Derrick et al.[3] The shifts introduced by the many-body calculation are considerable in the final results for nearly all IP's. Typically the shifts are between 1.5 and 2.0 eV, but they are smaller for the first two orbitals. The magnitude and nonuniformity of these shifts demonstrates the importance of taking into account electron correlation and reorganization for the valence IP's. No dramatic reversals have been found for these two molecules. But the accuracy of the calculated IP's which is about ±0.5 eV for these large molecules gives more confidence in the assignment than trusting Koopmans' approximation.

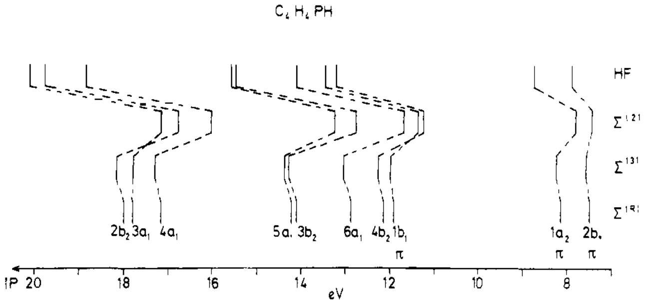

Figure 3. Calculated vertical ionization potentials of phosphole.

The final results for the phosphole molecule are given in Table VI and are graphically presented in Figure 3. All IP's are shifted to somewhat too low binding energies in the second-order calculation which is corrected for in the third-order result. The ordering of the first two IP's remains as in the HF approximation and it can be regarded as established that the first IP is due to ionization from the $2b_1(\pi)$ MO. It would require great deviations from the present guessed geometry to change this order. In the HF approximation the third MO is the $4b_2$ orbital. This, however, is changed in the many-body calculation (third order and renormalization) and the final results indicate that in the case of phosphole all the first three IP's may be due to ionization from the π orbitals. It would be the first molecule of this type where this occurs. For all other molecules investigated so far[29-31] there are one or more IP's due to σ-type orbitals placed between the IP's due to the π orbitals. But because of the guessed geometry one cannot be sure that this is going to be the case, it only represents an interesting possibility.

Table VII. Computation Times for the Different Steps of the Calculation (Times Refer to an IBM 360/91 Computer)

Step	Time	
	C_4H_4NH	C_4H_4PH
Integral evaluation, min	12.5	67
SCF iteration per step, min	0.45	0.9
Four-index transformation, min	13.5	29
Calculation of IP per orbital in second order for largest basis, sec	2	2
Calculation of IP per orbital in third order for basis set of 16 (19, 23) virtual orbitals, min	5-7	3-6
	(9-15)	(5-9)

Another reversal in the ordering of the IP's is found for the $2b_2$ and $3a_1$ IP's. In the HF approximation the $3a_1$ IP is larger than the $2b_2$ IP by about 0.3 eV, whereas in the final result the $2b_2$ IP is larger by about 0.2 eV. These IP's are so close together that it is not possible to decide on their relative ordering in particular since they have already fairly large binding energies. The small pole strength of the $3a_1$ IP is a strong indication that intense satellite lines should lie in the region of the principal line. This means that a different renormalization method than used here should be applied to decide the ordering of the $2b_2$ and $3a_1$ IP's. The $3b_2$ and $5a_1$ IP's are very close together as well, but they are shifted by a nearly equal amount in the many-body calculation so that a reversal of their ordering might be expected if the true geometry differs from the assumed one. Fairly large shifts of about 1.5 to 2.0 eV are again found for the majority of the IP's in the many-body calculation.

A summary of the computational expense of the various steps in the calculation is given in Table VII.

IV. One-Electron Properties

A number of one-electron properties has been calculated for the pyrrole and phosphole molecules. The calculations have been performed in the one-particle approximation. For pyrrole a number of properties has been measured[40-43] and theoretically calculated;[16,44] for phosphole we can only note the trends compared to pyrrole. The computed one-electron properties include dipole moment, second moments, quadrupole moments, third moments, octupole moments, charge density at the nuclei, average diamagnetic shielding at the nuclei, diamagnetic susceptibility, potential, electric field and electric field gradient at the nuclei, deuteron and ^{14}N quadrupole coupling constants, and asymmetry parameters. For a definition of these properties we refer to the article by Neumann and Moskowitz.[45] The calculations have been performed with the property package of the POLYATOM program system[46] as modified and adapted to the MUNICH program system. In Table VIII the results for the properties are listed together with experimental and other theoretical data. The conversion factors of Rothenberg and Schaefer have been used to convert from atomic units to units more frequently used by experimentalists.[47]

The dipole moment is about the same for pyrrole and for phosphole. The agreement with the experimental value for pyrrole is quite good. Wave functions calculated with basis sets of double ζ quality, which do not contain polarization functions, generally overestimate the dipole moment considerably. It is surprising that the dipole moment of pyrrole and phosphole is so much larger than the value for furan and has the opposite direction (positive end at the heteroatom); this must be due to the effect of the additional H atom bonded to the N atom which is positively charged. The experimental and theoretical values of the electronic part of the second moments, which measure the extent of the electronic charge cloud, are in good agreement with each other as is commonly the case for this property. The agreement between the two theoretical calculations of the quadrupole moment is good, but the agreement with the experimental quantity is only fair, particularly for the value of θ_{xx} which is considerably larger from experiment. The quadrupole moment tensor of phosphole has components of nearly the same magnitude as calculated for pyrrole. No experimental or theoretical results are available for the third moments and the derived octupole moments. These data are expected to vary sensitively with the quality of the wave function as has been found for the water molecule by Neumann and Moskowitz.[45] Pyrrole and phosphole give again very similar values. As expected all atoms in the phosphole molecule are considerably more shielded than in the pyrrole molecule; surprisingly the smallest difference is found for the H atom on the heteroatom. The atoms C_3 and C_4 are more shielded than C_1 and C_2 by only 3 ppm in pyrrole and 10 ppm in phosphole. H_3 and H_4 are more shielded than H_1 and H_2 by 1.7 ppm in pyrrole and by 8 ppm in phosphole. These data cannot be correlated with the results of the population analysis as has been found before for other heterocyclic molecules.[30,31]

The agreement of the theoretical and experimental values for the diamagnetic susceptibility tensor is satisfactory, the theoretical values lying within or just outside the experimental error limits. The potential at the nuclei is a rather insensitive quantity which can be seen from the uniformity of the values for equivalent atoms in the two molecules and for structurally different atoms within the same molecule. The electric field at the nuclei is related to the Hellmann–Feynman forces (multiplication by the nuclear charges). In their majority these forces are directed to compress the ring and shorten the CH bond length but they tend to stretch the C–N and the N(P)–H bond length. Whereas for pyridine[30] and furan[31] it was found that a large force was exerted on the heteroatom this force is of average magnitude in the case of pyrrole. The size of the forces in phosphole is about the same as for pyrrole which is surprising because of the guessed geometry of this molecule. From the electric field gradients at the nuclei the quadrupole coupling constants at the deuteron ($Q = 0.002\,796b^{48}$) and at the ^{14}N nucleus ($Q = 0.016b^{44,49}$) have been calculated. No theoretical or experimental data are known to the authors for the deuteron quadrupole coupling constants. In previous calculations they were found to be too large in absolute value but such that the asymmetry parameter was in reasonable agreement with experiment.[29,30] In the present case the asymmetry parameters are rather small except for the D_5 atom. For the atoms D_1 and D_3 the coupling constants are somewhat larger in absolute value for pyrrole than for phosphole and much larger (by more than a factor of 2) for D_5. The ^{14}N quadrupole coupling constants and the asymmetry parameter are in satisfactory agreement with experiment.[43] The improvement with respect to the calculation of Kochanski et al.[44] is considerable.

The localized molecular orbitals (LMO's) have been calculated by the method of Boys.[50] Pyrrole and phosphole give very similar results and the LMO's have the same structure as found for furan and thiophene. Localizing the orbitals of σ- and π-type symmetry separately one obtains a set of normal single bond orbitals and a set of localized π orbitals which essentially represent bonds between the atoms C_1 and C_3 (as well as C_2 and C_4) and a π-type lone-pair orbital on the heteroatom. This π-type lone-pair orbital is somewhat delocalized onto the neighboring atoms both in

Table VIII. One-Electron Properties for Pyrrole and Phosphole (Origin-Dependent Quantities are Given with Respect to the Center of Mass)

	C_4H_4NH	C_4H_4PH
	Dipole Moment, D	
μ	1.992 (1.74 ± 0.02;[a] 1.977[b])	1.935
	Electronic Part of Second Moments, 10^{-16} cm^2	
$\langle x^2 \rangle$	39.72 (38.6 ± 0.7[c])	46.16
$\langle y^2 \rangle$	39.50 (39.1 ± 0.7[c])	63.45
$\langle z^2 \rangle$	7.28 (7.5 ± 0.7[c])	9.12
$\langle r^2 \rangle$	86.50 (85.2 ± 2.1[c])	118.73
	Second Moments (Total), 10^{-16} cm^2	
Q_{xx}	−5.691	−7.343
Q_{yy}	−5.015	−6.364
Q_{zz}	−7.281	−9.116
	Quadrupole Moments, 10^{-26} esu cm^3	
θ_{xx}	2.195 (5.8 ± 1.6; 2.717[b])	1.906
θ_{yy}	7.065 (6.6 ± 1.2; 7.121[b])	8.960
θ_{zz}	−9.259 (−12.4 ± 2.3;[c] −9.837[b])	−10.866
	Third Moments, 10^{-24} cm^3	
R_{xxy}	0.683	0.551
R_{yyy}	2.746	2.798
R_{yzz}	0.488	0.371
R_{yrr}	3.917	3.719
	Octupole Moments, 10^{-34} esu cm^3	
Ω_{xxy}	−1.205	−2.322
Ω_{yyy}	4.755	6.797
Ω_{yzz}	−3.550	−4.475
	Charge Density, e/$a_0{}^3$	
$\langle \delta(r\text{-}C_1) \rangle$	119.913	119.923
$\langle \delta(r\text{-}C_3) \rangle$	119.931	119.948
$\langle \delta(r\text{-}H_1) \rangle$	0.3674	0.3667
$\langle \delta(r\text{-}H_3) \rangle$	0.3677	0.3653
$\langle \delta(r\text{-}N, P) \rangle$	194.698	2144.01
$\langle \delta(r\text{-}H_5) \rangle$	0.3344	0.3020
	Average Diamagnetic Shielding, ppm	
$\sigma^d(C_1)$	419.37	442.96
$\sigma^d(C_3)$	422.21	452.42
$\sigma^d(H_1)$	171.20	189.70
$\sigma^d(H_3)$	172.90	197.43
$\sigma^d(N, P)$	480.11	1089.45
$\sigma^d(H_5)$	179.07	190.40

	C_4H_4NH	C_4H_4PH
	Diamagnetic Susceptibility, 10^{-6} erg/(G^2 mol)	
χ_{xx}	−198.45 (−197.6 ± 2.1[c])	−307.87
χ_{yy}	−199.40 (−195.7 ± 1.9[c])	−234.51
χ_{zz}	−336.07 (−329.8 ± 2.5[c])	−456.03
	Potential at the Nuclei, au	
$\phi(C_1)$	−14.74	−14.72
$\phi(C_3)$	−14.69	−14.71
$\phi(H_1)$	−1.088	−1.082
$\phi(H_3)$	−1.062	−1.071
$\phi(N, P)$	−18.30	−54.14
$\phi(H_5)$	−0.964	−0.952
	Electric Field at Nuclei $\mathbf{E} = (E_x, E_y, E_z)$, au	
$\mathbf{E}(C_1)$	(−0.011, −0.024, 0)	(−0.005, −0.024, 0)
$\mathbf{E}(C_3)$	(−0.035, −0.013, 0)	(−0.026, 0.001, 0)
$\mathbf{E}(H_1)$	(−0.043, −0.058, 0)	(−0.039, −0.058, 0)
$\mathbf{E}(H_3)$	(−0.071, 0.023, 0)	(−0.073, 0.008, 0)
$\mathbf{E}(N, P)$	(0, 0.023, 0)	(0, −0.031, 0)
$\mathbf{E}(H_5)$	(0, 0.043, 0)	(0, 0.021, 0)
	Deuteron Quadrupole Coupling Constants, kHz	
$e^2q_{aa}Q/h(D_1)$	−113.1	−110.3
$e^2q_{bb}Q/h(D_1)$	240.2	233.4
$e^2q_{zz}Q/h(D_1)$	−127.1	−123.1
$\eta(D_1)$	0.058	0.055
$e^2q_{aa}Q/h(D_3)$	−109.5	−108.2
$e^2q_{bb}Q/h(D_3)$	238.2	233.8
$e^2q_{zz}Q/h(D_3)$	−128.7	−125.6
$\eta(D_3)$	0.081	0.074
$e^2q_{aa}Q/h(D_5)$	−102.4	−42.4
$e^2q_{bb}Q/h(D_5)$	242.5	108.4
$e^2q_{zz}Q/h(D_5)$	−140.1	−66.0
$\eta(D_5)$	0.157	0.218
	Quadrupole Coupling Constants for ^{14}N in Pyrrole	
$e^2q_{aa}Q/h(N)$	1.485 (1.24;[e] 2.341[f])	
$e^2q_{bb}Q/h(N)$	1.707 (1.43;[e] 2.916[f])	
$e^2q_{zz}Q/h(N)$	−3.192 (−2.67;[e] −5.257[f])	
$\eta(N, P)$	0.070 (0.071;[e] 0.109[f])	0.0035

Electric Field Gradients at Nuclei in Principal Axes Coordinates Relative to Each Nucleus $\mathbf{q} = (q_{aa}, q_{bb}, q_{zz})$ (au) and Rotation Angles α,[d] deg

	C_4H_4NH	C_4H_4PH
$\mathbf{q}(C_1)$	(−0.0733, −0.0144, 0.0877), α = 23.74	(−0.0901, −0.0378, 0.1279), α = 13.80
$\mathbf{q}(C_3)$	(−0.2199, 0.2113, 0.0087), α = 1.72	(−0.1411, 0.0786, 0.0625), α = 7.58
$\mathbf{q}(H_1)$	(−0.1722, 0.3656, −0.1934), α = 0.12	(−0.1679, 0.3552, −0.1873), α = 0.06
$\mathbf{q}(H_3)$	(−0.1667, 0.3625, −0.1959), α = 0.46	(−0.1647, 0.3559, −0.1912), α = 0.78
$\mathbf{q}(N, P)$	(0.3951, 0.4541, −0.8491), α = 0	(0.5119, 0.5155, −1.0273), α = 0
$\mathbf{q}(H_5)$	(−0.1559, 0.3691, −0.2132), α = 0	(−0.0646, 0.1650, −0.1004), α = 0

[a] Reference 43, experimental. [b] Reference 16, theoretical. [c] Reference 40, experimental. [d] The angles α are defined for the local coordinate systems in Figure 1 for both pyrrole and phosphole. [e] Reference 41, experimental. [f] Reference 44, theoretical.

pyrrole and in phosphole. The situation is very similar to the one encountered for furan and thiophene. If all MO's are localized together they mix and one obtains better localized orbitals than result from a separate localization for σ- and π-type orbitals. For both molecules the LMO's correspond to a structure with a single bond between the atoms C_1 and C_2 and between the heteroatom and the neighboring C atoms. The atoms C_1 and C_3 as well as C_2 and C_4 are linked by two digonally equivalent bond orbitals. The heteroatom has a considerably distorted lone-pair orbital in the case of pyrrole and a nearly pure π-type lone-pair orbital on the P atom which has smaller contributions from all atoms of the ring. The equivalence of the LMO's in phosphole is good, whereas in pyrrole the C–N and the C_1–C_3 bond orbitals are distorted. The lone-pair orbitals in both molecules are delocalized into the ring, but on the whole the structure looks very much like that of a diene.

V. Conclusions

The valence IP's of the pyrrole and the hypothetical phosphole molecule have been calculated by a many-body approach which includes the effect of electron correlation and reorganization beyond the HF approximation. The investigations are based upon ab initio wave functions which have been calculated with a basis set of Gaussian functions of double ζ quality. A number of one-electron properties have been calculated in the one-particle approximation and are in the majority in good agreement with available experimental and other theoretical results and in moderate agreement in the case of more sensitive properties (e.g., quadrupole moment). The order of the IP's is markedly different for the two molecules. The first two IP's from the ionization limit are due to MO's of π symmetry, but for pyrrole the a_2 IP is lower than the b_1 IP, whereas in phosphole the order is reversed. The same feature has been found in pyridine and phosphoridine, where it could be explained by the electron withdrawing or releasing property of the heteroatom. This is not possible in the present case because the charges on the heteroatom as measured by the population analysis are nearly identical with the ones found in furan and thiophene where a reversal of the sequence is not found in going from the O to the S compound. It thus appears to be a property of the P atom in heterocyclic molecules of the type investigated here. The other IP's have a different ordering in the two molecules too. The HF approximation is found to be correct for pyrrole concerning the ordering of the IP's. For pyrrole the ordering is $1a_2(\pi)$, $2b_1(\pi)$, $6a_1$, $4b_2$, $1b_1(\pi)$, $3b_2$, $5a_1$, $4a_1$, $2b_2$, $3a_1$. The present ordering disagrees with the assignment of Derrick et al.[3] with respect to the order of the $4b_2$, $1b_1$ IP's and of the $3b_2$, $5a_1$ IP's. For phosphole the orbital ordering in the HF approximation is $2b_1(\pi)$, $1a_2(\pi)$, $4b_2$, $1b_1(\pi)$, $6a_1$, $3b_2$, $5a_1$, $4a_1$, $3a_1$, $2b_2$, but in the many-body calculation the $1b_1$ IP moves to the first place in the third-band system. Because of the small difference of the $1b_1$ and $4b_2$ IP's the calculations should be repeated with the true geometry of the molecule when measured. With the present ordering phosphole would be the first molecule which we have calculated in this series where all π orbitals have lower binding energies than the σ-type orbitals. For most molecules there are one or more σ-type orbitals lying between the π orbitals. The agreement of the theoretical and experimental values for the IP's is very satisfactory for the majority of the cases (pyrrole). The experimental values are uncertain because of the bad overlapping of the bands, which does not permit an accurate determination of band maxima.

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