# Non-empirical Calculations of the Electronic Structure of Some Five-membered Ring Heterocycles containing Sulphur and Phosphorus: Thiophen and Phosphole

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A comparison of the electronic structures of thiophen and phosphole and their first row analogues furan and pyrrole has been made by a linear combination of gaussian orbital (LCGO) procedure. The LCGO procedure indicates a non-planar structure for phosphole itself, as found for the 1-benzyl derivative; this arises from an increase in $3s_P$ orbital contributions to the bonding in the pyramidal case. The low inversion barrier in phospholes has been interpreted by a valency force field, without reference to aromatic character. In both molecules the $3d$ orbitals behave as polarisation functions rather than strongly bonding functions. Phosphole has no resonance energy, and the π-levels $3b_1$ and $1a_2$ are reversed in binding energy order relative to thiophen. The ^1H n.m.r. spectra of simple phospholes have been compared with those of cyclopentadiene, rather than of thiophen.

IN previous papers we have reported non-empirical molecular orbital (MO) calculations of the electronic structure of various five-membered ring heterocycles containing oxygen and/or nitrogen.[1-4] Our policy has been to study a wide variety of heterocyclic molecules of related types with a standardised basis set (except for that of the heteroatom which inevitably must vary with the element); † in this way we hope to obtain strictly comparable data, and perhaps elucidate some of the finer differences in the electronic structure of the molecules. Differences could well be missed even with calculations using a larger basis set unless this standardisation of procedures is adopted.

(1)
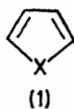
A logical extension of the earlier work was similar studies of phosphorus and sulphur heterocycles (1; X = PH or S). The primary objectives of the work are thus (a) to determine the degree of aromatic character of the ring system and where possible to derive a value for the resonance energy; (b) to study the role of added $3d_X$ orbitals in the second row elements [6] and compare these with polarisation functions reported earlier for the first row compounds (1; X = O or NH); [2] and (c) to discuss the variations in MO energy levels and to make predictions concerning the photoelectron spectrum of the phosphole system. Phosphole is as yet unknown, but various simple derivatives, e.g. 1-methylphosphole are well known. It is well known that 1-benzylphosphole

has a non-planar ring; [9] here we investigate whether the same is likely for the parent compound (1; X = PH) and comment upon the differences with pyrroles which are planar.[10] We note that the inversion barriers of phospholes are lower than phosphines,[11,12] and that this has been attributed to aromaticity in the (upper) planar state [11,12] leading to a smaller energy gap. We discuss this, and offer an alternative explanation.

METHODS

Orbital Basis.—The linear combination of gaussian orbital (LCGO) procedure was used. The orbitals were represented by a series of gaussian type functions (GTFs) identical with those used previously; [2,6-8] the orbitals $1s_H$, $1s_C$, $2s_C$, and $2p_C$ were represented by 3, 5, 2, and 3 s- or p-type GTFs respectively; the second row elements were represented by 6, 2, 2, 4, 2, and 1 GTFs for $1s_M$, $2s_M$, $3s_M$, $2p_M$, $3p_M$, and $3d_M$ respectively (M = S or P). The necessity of using six $3d$ functions (of types $3d_A$ where $A = xy$, xz, yz, x^2, y^2, and z^2) in order to preserve the three-fold symmetry in indexing sequences during the evaluation of electron repulsion integrals, was overcome by combining these six functions into linear combinations such that the usual ' chemical set ' with $A = xy$, xz, yz, $x^2 - y^2$, z^2 were produced together with a further orbital with $A = x^2 + y^2 + z^2 = r^2$; the latter is of s-type symmetry and is hereafter denoted as $3s'$ (as in our earlier work),[6-8] while the earlier five orbitals will continue to be called $3d$. Calculations with and without various combinations of the six functions, $3d/3s'$ were carried out, after integral evaluation, at the self-consistent field stage.

Gaussian Exponents and Atom Energies.—The ' best atom ' basis of the earlier work [1,3-5] yielded energies for the atoms (and their corresponding Hartree–Fock limiting

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† In our earliest work [1-5] we used a different, but closely related basis set, which had been optimised purely for the component atoms, rather than the present one which was optimised on small molecules carrying the appropriate atoms.[2] We have presented some results comparing the two basis sets earlier,[2] and further comments also occur here; briefly all work on the azoles [3] and azines [5] used the earlier ' best atom ' bases, and we have now standardised on the ' scaled basis ' of the latter type.[2,6-8]

[1] M. H. Palmer and A. J. Gaskell, *Theor. Chim. Acta*, 1971, **23**, 52.

[2] M. H. Palmer, A. J. Gaskell, and M. S. Barber, *Theor. Chim. Acta*, 1972, **26**, 357.

[3] S. Cradock, R. H. Findlay, and M. H. Palmer, *Tetrahedron*, 1973, **29**, 2173.

[4] M. H. Palmer, A. J. Gaskell, and M. S. Barber, *J. Mol. Structure*, 1972, **12**, 197.

[5] M. H. Palmer, A. J. Gaskell, and R. H. Findlay, *J.C.S. Perkin II*, 1974, 778.

[6] M. H. Palmer and R. H. Findlay, *Tetrahedron Letters*, 1972, 4165.

[7] M. H. Palmer and R. H. Findlay, *J.C.S. Perkin II*, 1974, 1885.

[8] M. H. Palmer and S. M. F. Kennedy, *J.C.S. Perkin II*, 1974, 1893.

[9] P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quinn, *J. Amer. Chem. Soc.*, 1970, **92**, 5779.

[10] M. H. Palmer ' Structure and Reactions of Heterocyclic Compounds,' Arnold, London, 1967.

[11] W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6205.

[12] A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6507.

values [13] in parentheses) are: $H(^2S)$, -0.4971 (-0.5000); $C(^3P)$, -37.6106 (-37.6886); $P(^4S)$, -340.0628 (-340.7190); $S(^3P)$, -396.6988 a.u. (-397.5050 a.u.) respectively; thus these gaussian bases already obtain $\geqslant 99.7\%$ of the Hartree–Fock free atom energies.[13] The scaling procedure, to improve these functions further by taking into account the molecular environment and described previously [2] for C and H, was extended to $CH_2=PH$ and $CH_2=S$ to obtain data for P and S.[7,8] The $3d$ exponents

Geometric Features.—Thiophen was studied at the experimental geometry.[14] The simplest phosphole derivative for which a full geometry has been given is 1-benzylphosphole.[9] This has a puckered ring with both P and CH_2 lying out of the hydrocarbon plane, and to opposite sides of it. We adopted this geometry for one series of computations on phosphole, and in the other we rotated both P and H to a coplanar arrangement with C_4H_4. In both cases the PH length was chosen to have the same relationship to

TABLE 1

Molecular energies for thiophen, phosphole, and phosphine

Basis set	sp	spd	$spd + 3s^1$	Ref. 9 ' No pol.'	' $+S3d$ '
Thiophen					
Total energy (a.u.)	$-550.075\ 05$	$-550.144\ 17$	$-550.191\ 43$	-550.923	-550.976
Atomisation energy (a.u.)	$-0.945\ 5$	$-1.014\ 62$	$-1.061\ 88$		
Relative energy (kJ mol^{-1})	0.0	-182	-306	0.0	-139
Resonance energy (kJ mol^{-1})	-124		-144		
Phosphole (pyramidal)	sp	$sp + 3s^1$	spd	$spd + 3s^1$	
Total energy (a.u.)	$-493.981\ 13$	$-494.023\ 71$	$-494.056\ 51$	$-494.099\ 21$	
Atomisation energy (a.u.)	$-0.990\ 39$	$-1.032\ 97$	$1.065\ 77$	$-1.108\ 47$	
Relative energy (kJ mol^{-1})	0.0	-112	-198	-310	
Resonance energy (kJ mol^{-1})	-54			-52	
Inversion barrier (kJ mol^{-1})	65.0	66.6	123.0	125.0	
Phosphole (planar)					
Total energy (a.u.)	$-493.956\ 38$	$-493.998\ 32$	$-494.009\ 70$	$-494.051\ 58$	
Atomisation energy (a.u.)	$-0.965\ 64$	$-1.007\ 58$	$-1.018\ 96$	$-1.060\ 84$	
Relative energy (kJ mol^{-1})	0.0	-110	-140	-250	
Resonance energy (kJ mol^{-1})	$+11$			$+73$	
Phosphine (pyramidal)					
Total energy (a.u.)	$-341.772\ 71$	$-341.816\ 32$	$-341.833\ 56$	$-341.877\ 33$	
Atomisation energy (a.u.)	$-0.218\ 33$	$-0.261\ 94$	$-0.279\ 18$	$-0.322\ 95$	
Relative energy (kJ mol^{-1})	0.0	-115	-160	-275	
Inversion barrier (kJ mol^{-1})	110	113	172	175	
Phosphine (planar)					
Total energy (a.u.)	$-341.730\ 82$	$-341.773\ 20$	$-341.768\ 15$	$-341.810\ 59$	
Atomisation energy (a.u.)	$-0.176\ 44$	$-0.218\ 82$	$-0.213\ 77$	$-0.256\ 21$	
Relative energy (kJ mol^{-1})	0.0	-111	-98	-210	

also were optimised as a function of total energy for these molecules.

Energy Analyses.—The *binding energy* is defined as the difference between the molecular total energy and the sum of the best atom values given above; thus we compare the total molecular energy and the atomic sum each with their optimised exponents; [1] since the $3d$ orbitals are vacant in the free atoms the binding energy inevitably rises as the $3d$ functions are added. The resonance energy was calculated by summation of the energies of the classical bonds in the molecule.[7,8] Thus if the total energies of methane and ethylene are E_{CH_4} and $E_{C_2H_4}$, then the bond energies E_{CH} and $E_{C=C}$ are given by $1/4$ E_{CH_4} and $E_{C_2H_4} - E_{CH_4}$ respectively. The energy of the classical single bond between sp^2 hybridised carbon atoms, required for the classical equivalent of the 3,4-bond in (1), was evaluated from a twisted buta-1,3-diene ($E_{C_4H_6}$) where the π-orbitals are mutually perpendicular; thus $E_{C_4H_6} = 2E_{C=C} + E_{C-C} + 6E_{CH}$. In the same way, the CX and XH bond energies (X = P or S) were evaluated from $CH_2=CH-XH_m$ where the XH bond lay perpendicular to the vinyl plane, and XH_n (X = S, $m = 1$, $n = 2$; X = P, $m = 2$, $n = 3$) total energies respectively.

PH_3[15] as the NH lengths in NH_3[16] and pyrrole.[1] As a simple test to find the effect of planarity on phosphorus we studied PH_3 at both the equilibrium [15] and planar geometries, assuming a fixed PH length.

RESULTS AND DISCUSSION

The molecular energies (Table 1) are given for all basis sets, the minimal sp, and those augmented by the $3s'$, the $3d$ (spd), or both ($spd + 3s'$) on sulphur or phosphorus. The orbital energies are subject to very small variation with basis set, and hence we record (Tables 2 and 3) only those for the largest ($spd + 3s'$) and smallest sets (sp).

Effect of Basis Set on Total Energies.—Addition of a single $3s'$ function to either S or P leads to an improvement in total energy by *ca.* 110 kJ mol^{-1} for both thiophen and phosphole (irrespective of whether the geometry of the latter is planar or pyramidal); a set of *five* $3d$ functions leads to further improvement, but is proportionately much smaller in effect when compared with $3s'$ function. The present results are in substantial agreement with an earlier (larger) [17] double zeta calculation

[13] E. Clementi, ' Tables of Atomic Functions,' Supplement to IBM Journal of Research and Development, 1965, vol. 9, p. 2.

[14] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1961, **7**, 58.

[15] C. A. Burrus, A. Jache, and W. Gordy, *Phys. Rev.*, 1954, **95**, 706.

[16] P. A. Helminger and W. Gordy, *Phys. Rev.*, 1969, **188**, 100.

[17] U. Gelius, B. Roos, and P. Siegbahn, *Theor. Chim. Acta*, 1972, **27**, 171.

on thiophen * in which the $3d$ set had an energy lowering of 0.053 a.u. (140 kJ mol⁻¹) compared with 0.069 a.u. (182 kJ mol⁻¹) of the present work. Indeed, the small differences between these two results are themselves

TABLE 2

Orbital energies for thiophen (eV)

sp Basis	$spd + 3s'$ Basis	Ref. 9 'No pol'
a_1	a_1	a_1
−2 492	−2 495	−2 503
−307.3	−307.1	−306.9
−307.0	−306.7	−306.2
−237.5	−237.9	−244.6
−179.8	−180.4	−181.7
−32.64	−32.07	−32.60
−26.96	−26.91	−27.13
−20.92	−20.75	−20.87
−19.51	−19.26	−19.29
−15.36	−15.12	−14.86
−12.99	−13.77	−12.82
b_2	b_2	b_2
−307.3	−307.1	−306.9
−307.0	−306.7	−306.2
−179.8	−180.4	−181.8
−27.06	−26.80	−27.24
−20.53	−20.37	−20.54
−16.25	−15.95	−16.05
−14.67	−14.62	−14.23
b_1	b_1	b_1
−179.7	−180.4	−181.6
−15.30	−14.96	−14.49
−10.25	−9.91	−9.52
a_2	a_2	a_2
−9.82	−9.57	−9.22

indicative of the role of the $3d$ functions as polarisation functions. That is, they improve, but do not change the gross nature of the bonding; in this way they are similar to $3d$ orbitals on carbon or $2p$ on hydrogen. For example, for furan and related molecules [2] we noted that five $3d_\sigma$ or $3d_\pi$ functions (one on each C and O) lead to energy lowerings of 376 and 364 kJ mol⁻¹ respectively, while addition of a set of 12 $2p$ functions to the hydrogen atoms of furan (three on each) lead to a similar improvement by 250 kJ mol⁻¹. In confirmation of the polarising role of the $3d$ orbitals in thiophen and phosphole, we note that the resonance energies are not greatly altered when $3d$ orbitals are added, although in principal a substantial contribution to the bonding by pd-hybridisation had earlier been postulated.[19]

In the light of the polarising nature of the $3d$ orbitals in thiophen and phosphole, it seems probable that comparisons with related molecules should more properly be made with the sp rather than $spd + 3s'$ bases. Thus for pyrrole, furan, phosphole, and thiophen, using con-

stant basis sets for hydrogen and carbon, we obtain binding (and resonance) energies as follows: C_4H_4NH, −2 785 (−149); C_4H_4O, −1 157 (−89); C_4H_4PH (planar), −2 536 (+11); C_4H_4PH (pyramidal), −2 601 (−54); thiophen, −2 483 (−124); benzene, −3 859 (−212); phosphorin (sp basis) −3 140 (−299); pyridine, −3 162 kJ mol⁻¹ (−222). It is clear that phosphole, whether non-planar or planar, is much less aromatic than either its first row analogue (1, X = NH) or its neighbour thiophen, and that it is much less aromatic than its six-membered ring counterpart phosphorin which is not

TABLE 3

Orbital energies for phosphole (eV)

Planar		Pyramidal	
sp	$spd + 3s'$	sp	$spd + 3s'$
a_1	a_1	a^1	a^1
−2 165	−2 168 $1s_P$	−2 165	−2 168
−306.2	−306.3 $1s_C$	−306.6	−306.5
−305.9	−305.9 $1s_O$	−305.9	−306.0
−197.6	−193.8 $2s_P$	−197.5	−197.9
−144.7	−145.5 $2p_P$	−144.4	−145.1
−30.71	−30.56 $2s_{C_2} + C_3$	−144.4	−145.0
−24.05	−23.92 $3s_P + 2s_{C_3}$	−31.24	−30.94
−20.14	−20.16 PH + CC	−24.51	−24.13
−18.63	−18.54 CC + CH	−20.26	−20.10
−15.46	−15.53 CH + CH	−18.72	−18.55
−13.64	−13.57 CC + CH	−15.26	−15.19
b_2	b_2	−14.33	−14.22
−306.2	−306.3 $1s_C$	−13.00	−12.94
−305.9	−305.9 $1s_C$	−9.43	−9.40
−144.6	−145.5 $2p_P$	a^{11}	a^{11}
−26.17	−26.15 $2s_{C_2-C_3}$	−306.6	−306.5
−18.84	−18.81 CP + CH	−306.9	−306.0
−15.19	−15.15 CH	−144.4	−145.1
−12.81	−12.88 CP	−26.49	−26.39
b_1		−19.08	−19.01
−144.6	−145.5	−15.53	−15.40
−13.90	−13.80	−13.05	−13.09
−8.22	−7.96	a_2	a_2
a_2	a_2	−9.38	−9.21
−9.10	−9.04		

greatly different from benzene or pyridine. We noted previously,[20] that there are clear indications from the average positions of the π-electrons of separation of the latter into a quartet and a pair, and that this separation is more apparent than in related compounds (1), other than furan. We discuss this aspect below.

Phosphole Ring Geometry and Inversion Barrier.—For all basis sets (Table 1), the non-planar form, based upon the 1-benzyl derivative is preferred to the planar form for phosphole itself. The $3d$ orbitals give some indication of destabilising the planar form, rather than stabilising it, as shown by the resonance energies planar: +11 (sp) and +73 ($spd + 3s'$ basis), pyramidal: −54 (sp) and −52 kJ mol⁻¹ ($spd + 3s'$ basis). This suggests that the $3d$ orbitals by allowing a further mechanism for delocalisation in the planar state are competing with an inherently non- or anti-aromatic system. The stabilisation of the pyramidal form although about twice that of

* Inevitably certain molecules reported in the present series of papers will be studied by others, and some will use larger basis sets. For thiophen two such calculations have been reported;[17,18] few details of one have been given [18] and it has been noted [17] that the conclusions in ref. 18 on the role of the $3d$ orbitals are unsound, since no separation of the six $3d$ functions into the $3s'$ and $3d$ functions was carried out; it is frequently found that the $3s'$ function contributes a large proportion of the total energy lowering.[6-8,17] It is appropriate to compare the results of the present work with those of ref. 17; our sp and spd bases are comparable with their 'no polarisation' and 'S3d' bases respectively.

[18] D. T. Clark and D. R. Armstrong, *Chem. Comm.*, 1970, 319.
[19] H. C. Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 174.
[20] M. H. Palmer, R. H. Findlay, and A. J. Gaskell, *J.C.S. Perkin II*, 1974, 420.

trans-buta-1,3-diene (-23 kJ mol^{-1}) is still very low in comparison with other aromatic systems (above).

On the assumption that the planar and non-planar geometries are reasonably accurate representations for the transition and ground states for inversion, the energy difference can be equated with the inversion barrier. As can be seen (Table 1), the values vary with the basis set; this is not unreasonable, since as we have noted that the $3d$ functions are polarisation functions, and as such will have differing roles in refining the wave-functions for the planar and non-planar forms; since there are no polarising functions on C or H the most logical course is to consider only the sp basis in this comparison; thus we expect the experimental barrier to be near the low end of the range 60—125 kJ mol^{-1}, and therefore rather less than that of the phosphine range 110—175 kJ mol^{-1}. Qualitatively these ranges are in the correct order for the experimental barrier in 1,2,5-trialkylphospholes (ca. 67 kJ mol^{-1}) and phosphines (156 kJ mol^{-1}) respectively.[11,12]

It has been suggested [11,12] that the low barrier to inversion in phospholes and 1,2-dimethylphosphindoles arises from increased $(2p$–$3p)\pi$ delocalisation in the transition state (TS) relative to the ground state (GS); thus the TS is lowered towards the GS by aromaticity in the former.[21] There is an element of circular reasoning here, and we find this ' explanation ' unacceptable. An aromatic system has an energy lower than that expected for a system of classical localised bonds, by definition. The non-planar state has poorer opportunities for conjugation and cannot be regarded as a strongly aromatic system itself and this is borne out by the present calculations. Thus if the planar state was aromatic it would be an energy minimum rather than a maximum; furthermore it would be the GS rather than the TS. For all that, the lower barrier in phospholes than in phosphines does require explanation and here we offer one based upon a valency force field.

The barrier restricting inversion, V_i, has been attributed to both tunnelling of the apical electron pair, and the deformation energy required to make the pyramid co-planar.[22-24] The former mechanism is complicated even for symmetrical pyramids XY_3, and is usually small and ignored for barriers larger than that in ammonia (24.3 kJ mol^{-1}).[22,23] A simple potential function V_i based upon the deformation term, which has been applied to a number of XY_3 systems, such as comparisons of NH_3 and PH_3 is given in equation (1). Here k_1 and

$$V_i = \tfrac{3}{2}k_1(\Delta l)^2 + k_\delta(\Delta\alpha)_2 \quad (1)$$

$$V_i = K(\Delta\alpha)^2 \quad (2)$$

$$V_\alpha = \tfrac{2}{3}K(\Delta\alpha)^2 \quad (3)$$

k_δ are the force constants for symmetrical stretching and bending of the XY bond and YXY angle respectively, and Δl and $\Delta\alpha$ are the changes in length XY and

angle YXY in the pyramidal to planar change. In the present work we assume that there are no changes in length, but it can be shown that the potential can anyway be rearranged to equation (2), by virtue of the known relationships between Δl and $\Delta\alpha$, and the molecular symmetry parameters.[22-24] The extension to cyclic asymmetric top molecules follows directly,[23] and if the ring angle at X is also constant as assumed in our phosphole model, then equation (2) is replaced by (3). Using the experimental geometry of 1-benzylphosphole for the parent molecular (except for the PH bond), $\Delta\alpha$ is $14.0°$; the value for K is 573 ± 42 kJ mol^{-1} radian^2 for phosphine.[22-24] The energy to flatten the $C_\alpha C_\alpha PH$ pyramid by movement of the hydrogen is 23 kJ mol^{-1} relative to 121 ± 12 kJ mol^{-1} for phosphine using the same procedure. For complete planarity it is still necessary to make coplanar the two planes $C_\alpha C_\alpha C_\beta C_\beta$ and $C_\alpha C_\alpha PH$, and this will absorb a further amount of energy. In view of the small height of the phosphorus atom from the hydrocarbon plane (0.21 Å in the 1-benzyl derivative) it is clear that this energy will also be small and a value of ca. 20 kJ mol^{-1} could be anticipated. Given the nature of the valence force field approximation it seems probable that this total, near to the experimental values for alkylphospholes, is explained. The barriers for alkylphosphines are very similar to those for phosphine itself.[22-24] It thus seems unnecessary to have recourse to aromaticity considerations to explain the low barrier in phospholes.

Pictorially it is clear since V_i is a function varying with the square of each deformation angle and that cyclic systems where one angle is constrained to small changes will have V_i smaller than for corresponding acyclic systems, unless the exterior bond(s) lie at a large angle from the local portion of the ring plane (i.e. the pyramid height is comparatively high). This latter circumstance occurs with aziridines and related species.[23]

Orbital Energies and Photoelectron Spectra.—For both thiophen and phosphole (Tables 2 and 3) there is a $1 : 1$ correspondence between the orbital ordering for all basis sets, and the shifts are small and generally to lower binding

TABLE 4

Population analysis for thiophen using various basis sets

| Total populations | | | | Ref. 9 'No | |
| | Basis | | | | |
	sp	spd	$spd + 3s'$	pol.'	' S $3d$ '
S	15.856 3	15.962 6	15.972 5	15.518	15.984
C(2), C(5)	6.239 3	6.172 2	6.165 3	6.568	6.245
C(3), C(4)	6.165 4	6.164 3	6.165 7	6.177	6.243
H(2), H(5)	0.826 6	0.836 2	0.836 8	0.733	0.751
H(3), H(4)	0.840 4	0.845 9	0.845 1	0.764	0.768

$3s' + 3d$ Populations ($spd + 3s'$ basis)

$3s'$	$3d_{x^2-y^2}$	$3d_{z^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$
0.344 6	0.009 3	0.018 6	0.079 8	0.027 3	0.011 4

energy as the $3s'$ and $3d$ orbitals are added. Such shifts [cf. the low populations of the $3d$ orbitals (Tables 4 and 5)] are a characteristic of polarisation functions, which

[21] W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, 1970, **92**, 1442.

[22] R. E. Weston, *J. Amer. Chem. Soc.*, 1954, **76**, 2645.

[23] G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. L. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 3396.

[24] C. C. Costain and G. B. B. M. Sutherland, *J. Phys. Chem.*, 1952, **56**, 321.

Table 5

Population analyses for phosphole and phosphine [a]

Phosphole (planar)

	P	C(2), C(5)	C(3), C(4)	H(2), H(5)	H(3), H(4)	H(1)
$1s + 2s + 3s$	5.068 6	3.070 5	3.059 8	0.852 9	0.851 5	0.825 9
$3s'$	0.221 7					
$(2p + 3p)\sigma(xy)$	5.803 1	2.054 7	2.057 7			
$(2p + 3p)\pi(z)$	3.690 6	1.079 5	1.050 1			
$3d_{\sigma+\pi}$	0.236 2					
Total	15.020 2	6.204 6	6.168 0	0.852 9	0.851 5	0.825 9
	$3d_{x^2-y^2}$	$3d_{z^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	
$spd + 3s'$ Basis	0.030 8	0.061 6	0.093 5	0.038 1	0.012 1	

Phosphole (pyramidal)

	P	C(2), C(5)	C(3), C(4)	H(2), H(5)	H(3), H(4)	H(1)
$1s + 2s + 3s$	5.254 6	3.080 2	3.073 1	0.853 4	0.850 0	0.877 9
$3s'$	0.258 8					
$(2p + 3p)_{xy}$	5.846 8	2.017 2	2.079 4			
$(2p + 3p)_z$	3.365 9	1.026 9	0.996 0			
$3d$	0.263 5					
Total	14.989 6	6.214 3	6.148 5	0.853 4	0.850 0	0.880 0
	$3d_{x^2-y^2}$	$3d_{z^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	
$spd + 3s'$ Basis	0.021 8	0.043 6	0.102 4	0.038 5	0.057 2	

Phosphine (pyramidal)

	P	H	(Planar)	P	H
$1s + 2s + 3s$	5.355 3	0.898 5		5.120 0	0.849 9
$3s'$	0.298 1			0.249 5	
$(2p + 3p)_{xy}$	5.942 8			5.931 3	
$(2p + ep)_z$	3.512 0			4.000 0	
$3d$	0.196 3			0.149 4	
Total	15.304 4	0.898 5		15.450 2	0.849 9

[a] In all cases the carbon atoms of the ring lie in the xy plane with the y-axis as C_2 symmetry axis. The notation of the $3d$ orbital follows standard usage (14) with, for example, $3d_{xy}$ having lobes in the xy plane but nodal in the x and y axes.
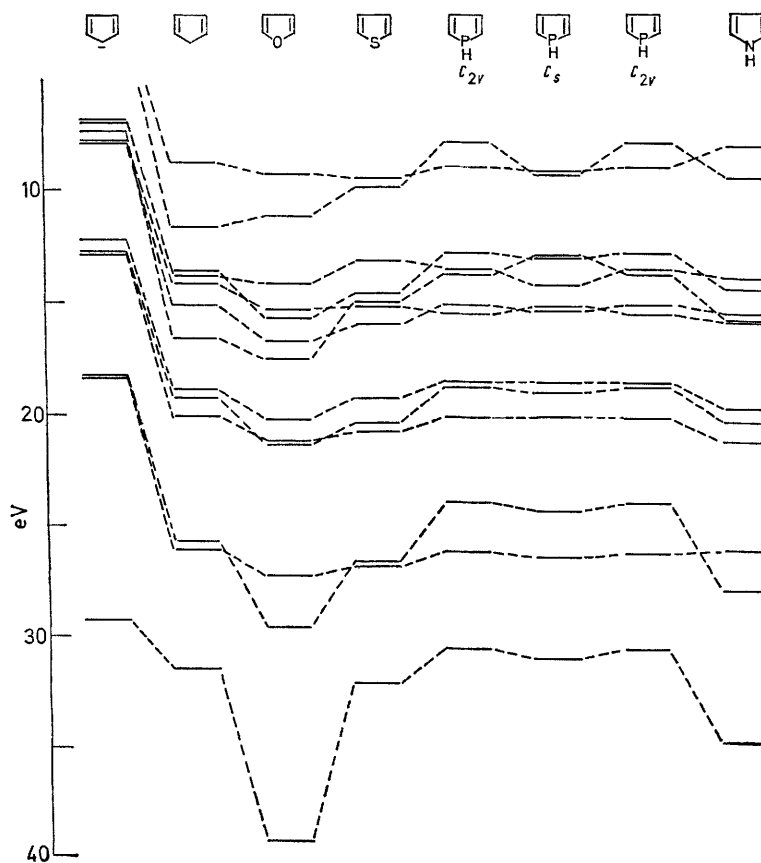
leads to better numerical agreement between the orbital energies and experimental ionisation potentials (IPs), where Koopmans' theorem is used in the correlation. Comparison of the thiophen data with one using a double zeta basis [17] shows that the latter orbital is shifted to lower binding energy by *ca.* 0.4 eV in the valency shell. In conclusion therefore, if the $3d$ orbitals have a major bonding effect, at least some of the orbitals would be strongly shifted to higher binding energy by the addition of the $3d$ orbitals; this is not observed with thiophen and phosphole and the role of these orbitals can be neglected from the following discussion on orbital energies. It is worth noting that this is not the case with either thiophen 1-oxide or 1,1-dioxide, where the $3d$ orbitals selectively stabilise certain orbitals.[25]

A comparison (Figure) of the orbital energies of thiophen and phosphole with their first row element analogues furan and pyrrole and with cyclopentadiene and the cyclopentadienyl anion shows that the valency shell region can be divided into five regions (A—E) and that orbitals always correlate within such a region. The innermost regions A and B are $2s$ levels, and as such are influenced by the electronegativity of the heteroatom and the consequent value of the free atom orbital energies; some relevant values of these orbital energies (eV) at the Hartree–Fock limit are: H, $1s$, 13.61; C, $2s$, 19.20; $2p$, 11.79; N, $2s$, 25.72; $2p$, 15.44; O, $2s$, 33.86; $2p$, 17.20; P, $3s$, 18.95; $3p$, 10.66; S, $3s$, 23.94; $3p$, 11.90 eV. It is interesting to note that the highest binding energy $2s$ level (A) in the cyclopentadienyl anion is only destabilised by *ca.* 2 eV relative to the corresponding orbital in the other compounds, whereas all its lower binding energy orbitals are destabilised by *ca.* 7—8 eV; a figure similar to the stabilisation (*ca.* 6 eV) achieved by a positive charge in the pyridinium and similar cations relative to pyridine and phosphorin.[26] The main changes in orbital ordering within the groupings C and D can be directly attributed to the varying $2p$–$3p$ free atom orbital energies and their contributions in the delocalised molecular orbital. That is, the σ-system does not change in nature through the series cyclopentadienyl anion, cyclopentadiene, furan, pyrrole, thiophen, and planar phosphole. As expected on the basis of π-electron theories, the principal differences in the series can be attributed to the π-orbitals. Symmetry requires that the outer π-orbitals in cyclopentadienyl anion are degenerate (e'' 1.080 eV not shown in the Figure). It is interesting to note that the splitting of this level in the C_{2v} molecules varies in the series thiophen < pyrrole < furan < cyclopentadiene, an order that parallels qualitative orders of aromatic character.[10] The splitting is not large (1.0 eV) in the planar form of

phosphole, but the σ–π mixing in the change of symmetry in going to the pyramidal case (C_s) leads to near degeneracy ($14a'$ and $8a''$). This change is achieved largely by an increase (1.44 eV) in binding energy for $3b_1$ since the $1a_2$ (C_{2v}) — $8a''$ (C_s) energy difference is only 0.17 eV; the $3b_1$ to $14a'$ stabilisation is achieved by the shift of some $3s_P$ density to the $14a'$ orbital which achieves some $3s_P + 3p_P$ character as a lone pair orbital. This is confirmed by the population analysis (Table 5 and below), where the character of $3b_1$ (C_{2v}; $3p_P$, 1.339 2 e) and $14a'$ (C_s; $3s_P + 3s_{P'}$, 0.232 7 e; $3p_P$ 0.877 1 e) also shows some shift of population to the carbon pseudo-π-orbitals.*

The inversion in order of $1a_2$ and $3b_1$ in planar phosphole is similar to that in selenophen and in phosphorin,[25] but contrasts with that of furan, pyrrole, thiophen, cyclopentadiene, *etc.* Thus in phosphole $3b_1$ contributes less to the molecular binding energy than the orbital $1a_2$ which is nodal at phosphorus. Thus the two most stable π-orbitals in phosphole are as in buta-1,3-diene. This is clearly at least a *non*-aromatic characteristic, and arises directly from the relative values of the $2p_C$ and $3p_P$ orbital energies. Similar considerations apply with As(^4S; $4p$, 10.05 eF), Se(^3P; $4p$, 10.96 eV), Si(^3P; $3p$, 8.08 eV), Al(^2P; $3p$, 5.72 eV), and B (^2P; $2p$, 8.43 eV) [13] heterocycles, where only a strongly electronegative substituent on the heteroatoms (1; $X = AsR$, SiR_2, AlR, or BR) will possibly lead to the b_1 orbital being stabilised relative to a_2; since the influence of a single in-plane substituent would be unable to achieve such an effect by a σ–π interchange on the atom, clearly the silicon system (1; $X = SiR_2$ where R is present in the π-system) may achieve such a stabilisation. Using the gas-phase photoelectron spectral data for the valency shell (He^{II}),[27] the $spd + 3s'$ basis set gave a linear correlation of the orbital energies (through Koopmans' theorem) if $IP_{exp} = 0.751\ IP_{calc} + 2.030$ eV with the overall standard deviation, and standard deviations in slope and intercept of 0.444, 0.019, and 0.378 respectively. If the data [28] from gas phase core ionisation potentials are included the equation becomes $IP_{exp} = 0.952\ IP_{calc} - 1.612$ with standard deviations (above order) of 1.367, 0.003, and 0.407 respectively. These results are only slightly changed with either the sp basis set, or that of Gelius *et al.*,[17] and are very similar to other correlations that we have established.[3,5,6-8] The order of the orbital sequence being the same as that of Gelius *et al.*[17] we support their assignment of the photoelectron spectrum which differs somewhat from that obtained from semi-empirical calculations.[27] The calculated separation of the C_{1s} levels (0.30 and 0.41 eV for the sp and $spd + 3s'$ basis respectively) is in good agreement with the deconvoluted gas-phase data.[28]

* In planar phosphole the CH bonding ($11a_1$) and $CC_π(2b_1)$ levels are nearly degenerate; on going to C_s symmetry mixing of these orbitals becomes allowed (giving $12a'$ and $13a'$). The new orbitals when treated as a pair are unchanged in energy relative to the planar state. In general, formation of the non-planar state leads to slight stabilisation of the orbitals through a lowering of energy; this is achieved by an increase in $3s + 3s'$ character at phosphorus by 0.223 1 e, rather similar to the planar-pyramidal character change in phosphine ($3s_P$ population increase 0.283 9 e).

[25] M. H. Palmer and R. H. Findlay, in the press.
[26] M. H. Palmer, R. H. Findlay, and A. J. Gaskell, *J.C.S. Perkin II*, in the press.
[27] P. J. Derrick, L. Asbrink, O. Edqvist, B.-O. Johnson, and E. Lindholm, *Internat. J. Mass Spectrometry Ion. Phys.*, 1971, **6**, 177.
[28] U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, *Physica Scripta*, 1971, **3**, 237.

Population Analysis.—In the smaller basis set calculations (*sp* basis of the present work and 'No pol.' of ref. 17), the total populations show sulphur positively charged relative to the α-carbons, and this is particularly (and excessively) large in the 'No pol.' calculation. The results of the larger basis set calculations from both studies are in virtually quantitative agreement, with the S atom nearly neutral. The Clark–Armstrong results [18] all have sulphur significantly positive, and it seems probable that this is a result of an unbalanced basis set; the 2*p*–3*p* orbitals were less adequately represented in what was otherwise a double zeta valence shell basis.

can rule out a significant effect of these populations on the geometry of the systems. The most significant differences in the planar and pyramidal forms of phosphole populations are the increase in (3s + 3s') population in the latter.

There is no strict comparison of the sub-totals of the $3p_P$ populations in phosphole between the planar and pyramidal states; however, it is clear that the $(3p_{x,y})_P$ populations are largely unchanged in the two forms, and since these levels are mainly responsible for the CP and PH σ-bonding this also is unchanged. The reduction in $(3p_z)_P$ in the pyramidal state relative to the

TABLE 6

Molecular properties for thiophen: calculated and experimental

	sp Basis	*spd* + 3*s'* Basis	Experimental	Ref. 9 'No pol.'	'S3*d*'
Dipole moment (D)	1.25	0.47	0.54	0.959	0.606
Quadrupole moment					
Q_{xx}	6.064	5.278	6.6 ± 1.5	6.784	6.536
Q_{yy}	−1.738	−0.046	1.7 ± 1.6	0.819	1.303
Q_{zz}	−4.320	−5.23	−8.3 ± 2.2	−7.593	−7.839
Diamagnetic susceptibility					
χ^d_{xx}	−288.6	−286.6	−284.8 ± 3.0	−286.6	−285.7
χ^d_{yy}	−228.2	−227.7	−225.7 ± 3.0	−226.9	−226.4
χ^d_{zz}	−444.8	−442.7	−438.1 ± 3.0	−440.6	−439.7
$\chi^d_{zz} - \frac{1}{2}(\chi^d_{xx} + \chi^d_{yy})$	−186.4	−185.6	−183.0 ± 3.0	−183.87	−183.6
Second moment					
x^2	161.8	161.5	159.0 ± 4.3	160.3	160.1
y^2	212.6	211.1	209.3 ± 4.6	210.6	210.1
z^2	30.33	30.13	30.4 ± 4.3	30.68	30.53
Potential (1/*r*) at nuclei					
r_S^{-1}	67.09	66.91		66.11	6.12
$r_{C_\alpha}^{-1}$	25.68	25.68		25.66	25.67
$r_{C_\beta}^{-1}$	25.09	25.10		25.04	25.05
$r_{H_\alpha}^{-1}$	11.14	11.15		11.19	11.19
$r_{H_\beta}^{-1}$	10.70	10.71		10.76	10.76

Consistent with these population variations, the dipole moment in ref. 18 (0.05 D) is the poorest of the results obtained.

The individual components of the thiophen population analysis also show a large amount of similarity between the present (*spd* + 3*s'*) and Gelius' larger calculations.[9] Previously we had noted [5] that transference of most of the d_σ population to the 3*s* orbital would lead to figures very similar to those of Gelius *et al.*,[9] at that time we were not able to separate the 3*s'* orbital from six *d* functions (3*s'* + 3*d*) in the population analysis, but the new data (Tables 3 and 4) show that this (1*s* + 2*s* + 3*s* + 3*s'*) is indeed the case. As expected almost all of the remaining $3d_\sigma$ population lies in the $3d_{xy}$ orbital whose lobe axes point closely towards the α-carbon atoms. The planar and pyramidal forms of phosphole show no significant differences in the total populations (Table 5); furthermore the population of the P–H atoms, common to both phospholes and phosphines, appears to be very similar in all cases. A further factor is the similarity in the trends of the 3*d* and 3*s'* populations between the two pairs of compounds; however, although the differences in each of these are common to both compound pairs, the total 3*d* population is low, and we

planar form reduces the amount of π-electron character of the system, which is already distorted by the movement of phosphorus from the hydrocarbon plane. This, the increase in $3s_P$ population, the inversion of order of $3b_1$ and $1a_2$, and the separation of the π-electrons into a quartet and pair in the planar state,[20] all point to a non-aromatic planar phosphole system. There is no driving force for phosphorus to change from its normal pyramidal states. Two forms can be envisaged (a) only H out-of-plane; (b) both P and H out-of-plane. Form (a) still allows considerable conjugation between the $3p_P$ component of the lone pair and the ring; however, as we have seen in the planar form, the orbital energy appears to be unsatisfactory for this to occur, since although its energy is close to that of carbon it remains heavily localised. However, a more probable destabilising effect on (a) is the absence of stabilisation of the system by interaction of the $3s_P$ with both the σ- and π-system when only hydrogen is out-of-plane (such a mild perturbation is unlikely to lead to much σ–π mixing). Thus in form (b) the $3s_P$ component is capable of interacting with both σ- and π-systems, leading to further stabilisation as detected in the resonance energy calculations.

Some Consequences of the Non-aromaticity of Phosphole.

—A recent study [29] of the Faraday effect in 1-butyl-phosphole and its C-methyl derivatives showed that the rotations are *lower* than those calculated assuming a pure localised model; an aromatic compound would produce *higher* rotations. Furthermore, C-methylation of phospholes leads to a blue shift of the first u.v. transition, more consistent with a butadiene than an aromatic system similar to pyrrole.[29] Similar conclusions have recently been drawn [30] by photoelectron spectroscopy, where 1-phenylphosphole gives two bands at 8.45 and 9.25 eV of equal intensity. In contrast 1-phenyl-pholan has two IPs at 8.35 and 9.30 eV with intensities 1 : 2 respectively.[30] The position of the higher IP in each case was assigned to the $3e_g$ π-system of the phenyl group (cf benzene 9.24 eV), while the lower IP was ascribed to near degeneracy of n and π levels of the

similar conditions, and thus it is difficult to draw significant conclusions about these shifts in view of the strong solvent effects that are often observed with heterocycles.[35] The coupling constants are less susceptible to solvent effects and in Table 7 we assemble data for some relevant species (1; X = O, S, NH, PMe, and CH_2). As in the six-membered rings the value of $J_{2,3}$ decreases with the electronegativity of the heteratom, while the value of $J_{2,5}$ decreases similarly in the series (1; X = O, S, and NH). However the values of $J_{2,5}$ in (1; X = PMe and CH_2) do not fit into this series, and also it is worth noting that away from the direct influence of the heteroatom (PMe or CH_2) the values of the coupling constants $J_{2,4}$ and $J_{3,4}$ are very similar, and in the case of $J_{3,4}$ very different from the other members of the series (1; X = O, S, and NH). We consider

TABLE 7

Proton resonance in five-membered ring heterocycles

(1; X = PMe) [a] J/Hz		(1; X = CH$_2$) [b]	(1; X = NH) [c]	(1; X = S) [d]	(1; X = O) [e]
2,3(=AB)	7.24	5.06	2.734	4.92	1.75
3,4(=BB')	1.96	1.94	3.632	2.95	3.3
2,4(=AB')	1.12	1.09	1.365	1.32	0.85
2,5(=AA')	3.01	1.94	1.858	3.45	1.4

[a] Ref. 34. [b] Ref. 36. [c] Ref. 37. Very similar values are given in ref. 38. [d] Ref. 39. [e] Ref. 40.

phosphole ring in the former, and only the n-level in the tetrahydro-derivative. The present calculations support the assignments [30] in the phosphole, since $14a'$ (n) + $8a'$ (π) are predicted to be nearly degenerate at 9.40 and 9.21 eV respectively in the pyramidal form of the parent molecule. We noted above that the same type of reversal seems probable between (a) pyridine ($1a_2$ and $2b_1$) and phosphorin ($1a_2$ and $3b_1$) and (b) thiophen ($1a_2$ and $3b_1$) and selenophen ($1a_2$ and $4b_1$) both from non-empirical calculations [26,31] and photoelectron spectroscopy.[32,33]

The ^{1}H n.m.r. spectrum of 1-methylphosphole has been compared with that for thiophen, and it has been suggested [34] that both sets of chemical shifts indicate a ring current, and hence aromaticity. Unfortunately there is no precise data for the chemical shifts of the series (1; X = O, S, NH, PMe, and CH_2) [34-40] under

that these couplings constitute evidence that 1-methylphosphole (and hence the parent ring system) is more akin to cyclopentadiene than to the other members (1; X = O, S, and NH), and is thereby non-aromatic. A comparison with the ^{1}H n.m.r. spectrum of buta-1,3-diene [42] is not satisfactory in view of the transoid nature of the latter, while cyclohexa-1,3-diene shows [43] coupling constants (using the same numbering as in Table 7) of $J_{2,3}$ (= J_{AB}) 9.42, $J_{3,4}$ (= $J_{BB'}$) 5.14, $J_{2,4}$ (= $J_{AB'}$) 1.06, and $J_{2,5}$ (= $J_{BB'}$) 0.91 Hz. One obvious feature here is that $J_{2,3}$ and $J_{3,4}$ are sensitive to the ring angles, and to the CX length. 3-Ethoxycarbonylphosphole has a ^{31}P resonance * further to low field and it is a less stable molecule than 1-methylphosphole.[44] This latter observation is in contrast to pyrroles where electron-donating groups destabilise the ring, while acceptors do not; [10] this suggests that 3-ethoxycarbonylphosphole is either

* The ^{31}P resonances in phospholes and related species [34,41] are anomalous; thus the resonances (relative to 85% H_3PO_4) of 3-methylphospholen (+15.2), 1-methylphosphole (+8.57), 3-ethoxycarbonylphosphole (−3.00), ethyl(divinyl)phosphine (+20.8), and trivinylphosphine (+20.7 p.p.m.) show that the cyclic compounds lie to lower field than the acylic species in all cases. This suggests that the contribution from the vinyl groups in the latter series is dependent upon average, non-planar forms.

[29] M. F. Bruniquel, J. F. Labarre, and F. Mathey, *Phosphorus*, 1974, **3**, 269.
[30] W. Schafer, A. Schweig, G. Markl, H. Hauptmann, and F. Matley, *Angew. Chem. Internat. Edn.*, 1973, **12**, 145.
[31] R. H. Findlay, unpublished results.
[32] H. L. Hase, A. Schweig, H. Hahn, and J. Redoff, *Tetrahedron*, 1973, **29**, 469.
[33] W. Schaefer, A. Schweig, S. Gronowitz, A. Taticchi, and F. Fringnelli, *J.C.S. Chem. Comm.*, 1973, 541.
[34] L. D. Quin, J. G. Bryson, and G. C. Moreland, *J. Amer. Chem. Soc.*, 1969, **91**, 3308.

[35] T. J. Batterham, ' N.M.R. Spectra of Simple Heterocycles,' Wiley, New York, 1973.
[36] M. Barfield and B. Chakrabarti, *J. Amer. Chem. Soc.*, 1969, **91**, 4346.
[37] H. Fukui, S. Shomokawa, and J. Sohma, *Mol. Phys.*, 1970, **18**, 217.
[38] E. Rahkamaa, *Mol. Phys.*, 1970, **19**, 727; *Z. Naturforsch.*, 1969, **24a**, 2004.
[39] A. Kergornard and S. Vincent, *Bull. Soc. chim. France*, 1967, 2197.
[40] G. S. Reddy and J. H. Goldstein, *J. Amer. Chem. Soc.*, 1962, **84**, 583; R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.
[41] J. J. Breen, J. F. Engel, D. K. Myers, and L. D. Quin, *Phosphorus*, 1972, **2**, 55.
[42] A. V. Cunliffe and R. K. Harris, *Mol. Phys.*, 1967, **13**, 269; R. H. Hobgood and J. H. Goldstein, *J. Mol. Spectroscopy*, 1964, **12**, 76.
[43] M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, 1969, **91**, 6325.
[44] L. D. Quin and S. G. Borleske, *Tetrahedron Letters*, 1972, 299.

just a conjugated olefin, or possibly that the electron-attracting properties of the substituent enforce planarity, with destabilisation of the ring leading to polymerisation. *It is perhaps worth* noting that the absence of P–H coupling in nickel chloride complexes of phospholes has been attributed to loss of the phosphole (localised) lone pair in complex formation.[45] The recent demonstration [46] that base catalysed cleavage of quaternary phospholes proceeds more rapidly than either their mono- or di-benzoderivatives, or non-conjugated-phosphonium salts has been attributed to either aromatic stabilisation of the phosphole product, or desta-bilisation of the quaternary phospholes;[46] the present work suggests the latter. There is a need for accurate thermochemical data for simple phospholes; earlier data on pentaphenylphosphole and 9-phenyl-9-phosphafluorene is incomplete owing to the necessity to make assumptions on latent heats of sublimation and other data.[47] However, it seems improbable that conclusions based on the pentaphenyl compound could be extended to simple phospholes in view of the degrees of rotational freedom within the molecule. The present work does not rule out some aromatic character in radical anions derived from 1-substituted phospholes and alkali metals; these last molecules show hyperfine coupling not too dissimilar from the corresponding phosphorins.[48] We recently reported that phosphorin shows considerable aromatic character.[26]

Conclusions.—(a) *Thiophen.* Bearing in mind the compromise in basis set necessary to achieve computations on very large molecules with a standard basis set, the present results compare very satisfactorily with those of Gelius *et al.*[17] Furthermore this comparison can be extended to a range of molecular properties evaluated from the wave-function (Table 6). Only in the case of the quadrupole moment does the double zeta calculation [17] make a fundamental difference to the results, and in this instance it leads to much better agreement with experiment. We have noted previously that the quadrupole moment requires a much more flexible basis than many quantum mechanical operators.[20]

(b) *Phosphole.* The present work clearly demonstrates that phosphole itself should be non-planar, as is the 1-benzyl derivative. It clearly has little or no resonance energy in either the planar or pyramidal states. This does not of course preclude its preparation, although it would presumably show diene character and hence perhaps be first isolated as a dimer, and in common with other phosphines be air-sensitive. There seems no reason to postulate an aromatic transition state to explain the low energy barrier to inversion in phospholes.

[45] L. D. Quin and J. G. Bryson, *Phosphorus*, 1973, **2**, 205.

[46] W. B. Farnham and K. Mislow, *J.C.S. Chem. Comm.*, 1972, 469.

[47] A. F. Bedford, D. M. Heinekey, I. T. Millar, and C. T. Mortimer, *J. Chem. Soc.*, 1962, 2932.

[48] E. H. Braye, I. Caplier, and R. Saussez, *Tetrahedron*, 1971, **27**, 5523; D. Kilcast and C. Thomson, *ibid.*, p. 5705.