The Electronic Structure of Conjugated Molecules. Non-empirical Calculations for the Benzenium, Pyridinium, Pyrylium, and Thiopyrylium Cations and a Comparison of the Last with Phosphorin

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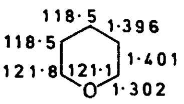
Non-empirical calculations on the title compounds and of the allyl carbonium ion are reported. For the second row compounds (1a and g), the role of the 3*d*-orbitals is that of polarisation functions rather than strongly bonding orbitals. The orbital energies of all the cyclic cations can be correlated directly with benzene and phosphorin, such minor rearrangements of orbital ordering that occur can be readily interpreted in terms of the heteroatom orbital energies. Support for the highest occupied orbital sequence of binding energies in phosphorin, $3b_1 < 1a_2 < 13a_1 < 8b_2$, as suggested by Schweig is given. The population analyses for the compounds are discussed. The hydrogen atoms absorb much of the positive charge in the cations (1a—e). The internal electric fields arising from the populations are evaluated, and compared with the observed chemical shifts; the anomalous shifts in the thiopyrylium cation (1a) are attributed to ring current effects, which are substantial in (1a) but probably much smaller or absent in the other cations, as evidenced by the dissociations of the π-electrons into well separated pairs. Some reactions of the second row compounds arise directly from the molecular orbital ordering and are discussed.

In previous papers [1-6] we have reported non-empirical molecular orbital calculations of the electronic structure of five- and six-membered ring heterocycles containing oxygen and/or nitrogen. More recently we extended this work to the corresponding compounds containing a second row element,[5a,c,6] particularly phosphorus or sulphur. Special interest attaches to these latter types since the question arises whether the 3*d* orbitals on P or S, and vacant in the free atom, are utilised in molecular ground states; we have briefly reported [5a] the conclusion that the 3*d* orbitals of ion (1a) appear to behave as polarisation functions rather than bonding orbitals in the normal chemical sense and this appears to be true for several sulphur heterocycles.[5c,6]

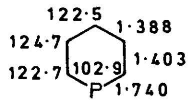
The objective of the present work is to expand the earlier results for phosphorin and the thiopyrylium cation (1a) [5a] and compare them with the pyrylium (1b), benzenium (1c), pyridinium (1d), and *N*-methylpyridinium cations (1e). Although the stability of the quaternary nitrogen compounds (1d and e) is not unexpected, the apparently permanent stability of the cations (1a and b) is unusual for sulphur and oxygen compounds. The benzenium cation is much less stable but has been observed by n.m.r. spectroscopy in strongly acid solutions of benzene,[7] and in the gas phase.[8] We have reported results for pyridine (1f) previously,[4b] and now we include parallel computations on phosphorin (1g) in order to compare not only first and second row cations, but also compare these with their corresponding neutral compounds. Only in the case of the benzenium cation (1c) [9] and phosphorin (1g) [10] have previous non-empirical

(1)

a; X = S$^+$
b; X = O$^+$
c; X = CH$_2^+$
d; X = NH$^+$
e; X = NMe$^+$
f; X = N
g; X = P
h; X = CH



(2)



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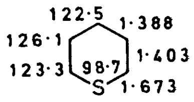

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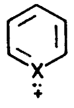

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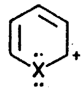
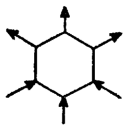


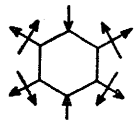
(6)

(7)

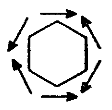
(8)



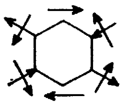
(9) e_{1uA}



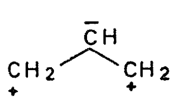
(10) e_{1gA}



(11) b_{2u}



(12) e_{1gB}



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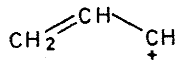

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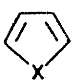

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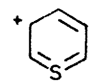

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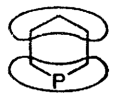

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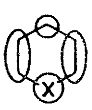

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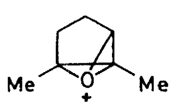

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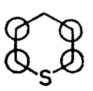

(19)

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[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 (*a*) *Theor. Chim. Acta*, 1972, **26**, 357; (*b*) *J. Mol. Struct.*, 1972, **12**, 197.

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[9] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 6901.

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calculations appeared, although investigation of some of the compounds by semi-empirical means has occurred. We shall refer to some of those calculations during the course of this paper.

METHODS

The Orbital Basis.—We used the same basis sets as in our other recent work;[2-6] these represent a compromise between length for near to Hartree–Fock single configuration accuracy, and the ability to carry out computations on some quite large systems. Thus the orbitals are represented by gaussian type functions (GTFs) in the linear combination of gaussian orbital basis (LCGO) as follows: $1s_H$, $1s_M$, $2s_M$, and $2p_M$ by 3, 5, 2, and 3 *s*- or *p*-type GTFs respectively for M = C, N, O, while the second row elements were represented by 6, 2, 2, 4, 2, and 1 GTFs for each of $2s_M$, $2s_M$, $3s_M$, $2p_M$, and $3d_M$ where M = S or P. The present set of gaussian functions are seen to be satisfactory in number of each type ($1s_C$, $2s_C$, *etc.*) when the energies of the current series of atoms are compared with the Hartree–Fock limiting values (in parentheses):[11] H(2*s*) −0·4971 (−0·5000), C(^{3}P) −37·6106 (−37·6886), N(4*s*) −54·2754 (−54·4009), O(^{3}P) −74·6121 (−74·8090), P(^{4}S) −340·0628 (−340·7187), S(^{3}P) −396·6988 (−397·5050) a.u. In all cases the present functions give >99·7% of the limiting values. In order to better mimic the molecular environment, the valency shell orbitals were further optimised for radial character using a series of small model molecules, CH_4, C_2H_4, H_2O, H_2S, PH_3, CH_2S, CH_2PH, *etc.* as described previously,[2a,5c] a concurrent series of optimisations of the 3*d* exponents being carried out for S and P using these molecules.

As usual the computations use np_x, np_y, and np_z orbitals (n = 2 or 3) and six 3*d* functions ($3d_A$) given by $A = xy, xz, yz, x^2, y^2$, or z^2. The latter six functions were contracted[12] to the normal chemical set (hereafter called 3*d*) of five $3d_A$ functions where $A = xy, xz, x^2 - y^2$, and z^2, and a further 3*s* function (hereafter denoted as 3*s*′) corresponding to $3d_A$ with $A = x^2 + y^2 + z^2 = r^2$. It should be noted that some authors (*e.g.* ref. 13) using an LCGO basis, fail to make this separation of the 3*s*′ function from the six 3*d* gaussian orbitals; whilst the separation does not alter (a) the total molecular energy or (b) the total electron density at any atom, it *does* alter most markedly the population of the chemical set of 3*d* orbitals. This occurs since for most molecules the 3*s*′ population is greater than the sum of all five 3*d* orbitals.[5a,c,6] As noted elsewhere,[14] it is thus possible to record erroneous conclusions as to the extent of the 3*d* orbital participation in the bonding of a particular molecule.

Molecular Energy Analysis.—The molecular atomisation (or binding) energy is the difference between the molecular total energy and the sum of the atoms, each in their ground states; the energies of the latter are given above. The atomisation energy of the ions is based upon similar summations of atom and ion energies, and the appropriate choices of which atoms are to be summed as neutral or ionic species is made as follows; the experimental ionisation potential (IP) of the free atoms, with those calculated with the same basis in parentheses are: H, 13·60 (13·52); C, 11·3 (10·80); O, 13·61 (13·26); and S, 10·36 (9·5) eV respectively. Thus we can assign the ease of formation of positive ions as follows $S < C < H, O$; the atomisation energies for cations (1b and a) are then based upon the difference in total molecular energy and (5H + 4C + C$^+$ + O) and (5H + 5C + S$^+$) respectively.

Molecular Geometries.—The benzenium cation was based upon benzene. The pyridinium cation was represented by that of the nitrate,[15] while the pyrylium cation was constructed as in (2) from it. The simplest phosphorin derivative for which a full geometry has been published is the 2,6-dimethyl-4-phenyl compound;[16] these data were used in the present work with appropriate C–H bonds (1·08 Å). The thiopyrylium cation (4) was based upon this and related sulphur and phosphorus compounds.[17] All C–H distances were taken as 1·08 Å unless known to be otherwise; the N–H distance in the pyridinium cation (1d) was optimised by minimisation of the molecular total energy, yielding an optimum value of 1.13 Å.

σ and π Electron Configurations and Populations.—All the molecules [except (1e)] have C_{2v} symmetry with electrons in the $(a_1 + b_2)\sigma$ and $(b_1 + a_2)\pi$ representations respectively. The *N*-methyl compound (1e) of C_s symmetry was chosen to have one CH_3 hydrogen in-plane, while the anti-symmetric combination of the other two is of π-symmetry. In all cases the rings lie in the *xz* plane with *z* as the symmetry axis. The number of π-electrons in the ground state is 8 (1a, e, or g) and 6 (1b—d, or f). Since the molecular charge increases the binding energy of the occupied orbitals the first virtual orbital (LUMO) of each representation is often also of negative energy, and as such indicates the ease of reduction of the molecule. This is shown in parentheses in Tables 2 and 3.

In the discussion of the population analyses below, we consider the total populations, and the net atomic populations obtained by subtraction of the free atom total population from the former. The distribution of the unit positive charge in the molecule is of considerable interest, in relation to the traditional canonical forms (5)—(7).

Cations (1a—c) are nominally derived from the corresponding radical C_5H_5X by an ionisation process [equation (1)]. The doublet ground state of $C_5H_5X^\bullet$ has the 7 π electron representation (8) and it is one of the π electrons which is ionised [equation (1)]. Therefore in the attempt to estimate the contributions of (5)—(7) we assign the positive charge to the π-system, and for (1a) the separate atomic populations (σ and π) are C, 5 and 1; S, 12 and 4 respectively. In contrast the pyridinium species (1d and e) are formed by addition to the nitrogen lone pair and hence the positive change is in the σ-system, and the partial atomic populations at nitrogen are σ, 6; π, 1.

$$C_5H_5X^\bullet \longrightarrow C_5H_5X^+ + e \qquad (1)$$

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[15] A. J. Serewicz, B. K. Robertson, and E. A. Meyers, *J. Phys. Chem.*, 1965, 1915.

[16] J. C. J. Bart and J. J. Daly, *J. Chem. Soc. (A)*, 1970, 567; *Angew. Chem. Internat. Edn.*, 1968, **1**, 811; an incomplete analysis of the microwave spectrum, with a considerable number of assumptions, has been reported by R. L. Kuczkowski and A. J. Ashe, *J. Mol. Spectroscopy*, 1972, **42**, 475.

[17] W. Gordy and R. L. Cook, 'Microwave Molecular Spectra,' Wiley, New York, 1970.

RESULTS AND DISCUSSION

Table 1 gives the results of computations on (1a—e, g) for all basis sets; some of these for (1a and g), *e.g.* $sp + 3s$, are deliberately unbalanced, but are intended to show the constant increments in energy as the basis set is increased by the addition of $3d$ and $3s'$ functions. In order to avoid excessive numbers of Tables we record the orbital energies (Table 2) and the population analyses (Table 3) for the molecules (1a and g) using only the smallest (sp) and longest basis sets ($spd + 3s'$); in all cases the intermediate sets produce values between those recorded, and there are no changes in constitution of the orbitals from different sets, and no changes in population beyond those anticipated by interpolation.

TABLE 1

Molecular energies

		Allyl cation	Benzenium cation	
Total energy		−115·67642	−230·37393	
Atomisation energy		−0·75629	−1·62821	
		Pyridinium cation	*N*-Methylpyridinium cation	
Total energy		−246·07615	−284·93683	
Atomisation energy		−1·16259	−1·41866	
	Pyrylium cation	Thiopyrylium cation		
Basic		*sp*	*spd*	*spd* + 3*s*′
Total energy	−266·06431	−588·14487	−588·23031	−588·27773
Atomisation energy	−1·31056	−0·99593	−1·08137	−1·12879
Relative energy (kJ mol^{-1})		0·0	−224	−349
	Phosphorin			
Basic	*sp*	*sp* + 3*s*′	*spd*	*spd* + 3*s*′
Total energy	−531·79672	−531·84046	−531·86186	−531·90524
Atomisation energy	−1·19549	−1·23923	−1·26063	−1·30401
Relative energy (kJ mol^{-1})	0·0	−115	−171	−285

The results of orbital energies and populations (Tables 1—3) for the thiopyrylium cation and phosphorin vary according to the basis set, and before we can compare and contrast these two with the other molecules (1b—f) of the series, it is necessary for us to assess these differing bases, and to decide whether any one basis set is superior to the others, or which properties are best represented by a particular basis set. Thus initially we discuss the question of $3d$ orbital participation on sulphur and phosphorus in (1a and g).

Role of 3d *and* 3s′ *Orbitals*

(a) *Molecular Energies*.—Comparison of various columns in Table 1 shows that addition of the $3s'$ orbital to S or P (1a or g) leads to a lowering of total energy by *ca.* −120 kJ mol^{-1}, while the five $3d$ orbitals ($3d^5$), although more variable in the two molecules (1a and c) produce a rather larger total effect -200 ± 30 kJ mol^{-1}. The latter is however less than twice that of a single $3s'$ function. In this respect the results are effectively identical to those found [5a,e] previously; the results were, thiophen: $3s'$, −126; $3d^5$, −180; 1,2- and 1,3-dithiolium cations: $3s'$, −130; $3d^5$, −200; and the centre S atom of thiathiophthen: $3s'$, −130; $3d^5$, −150 kJ mol^{-1}. Furthermore the effects are not substantially different from energy increments arising from the addition of a single $3d$ function to oxygen and one to each carbon atom in furan,[2a] which are $3d$, −126 and $3d$ −114 kJ mol^{-1}. Also for that molecule, the addition of a set of p-orbitals to each hydrogen atom (*i.e.* 12 functions in all) leads to a lowering in total energy of −250 kJ mol^{-1}. Thus since the effects in the present molecules are only slightly larger than those in furan, we are forced to conclude on an energy basis, that the $3d$ orbitals are *largely* polarisation functions in phosphorin (1g) and the cation (1a), as they are in furan, pyrrole, *etc.*

(b) *Population Analysis*.—The total $3d + 3s'$ populations for the P and S atoms of (1a and g) are *ca.* 0·5 e. This is largely made up to two terms, $3s'$ (*ca.* 60% of the total) and $3d_{xz}$ where the atomic orbital lobe maxima point closely along the C–P and C–S axes. The addition of the $3s'$ total to the corresponding sum of ($1s + 2s + 3s$) largely reduces the difference between the sp and ($spd + 3s'$) results.

(c) *Conclusions*.—There seems little doubt both on an energy and population basis, that the $3d$ orbitals are polarisation functions rather than strongly bonding orbitals in the LCAO sense. They add a refining effect to the wave function, which would diminish in importance if a much larger, but presently impracticable, basis set had been used. The bonds are modified slightly by their presence, but not changed in type and there is no evidence of pd-hybridisation as had earlier been suggested for thiophen.[18] Although we may have refined the wave function near the S or P atom, the absence of polarisation functions elsewhere in the molecule leaves these positions less well represented in the LCAO system. Any property which thus depends upon the electon distribution in the molecule as a whole (*e.g.* the electric dipole moment) will therefore be badly represented in an unbalanced system, as the $spd + 3s'$ system undoubtedly is; in contrast, local properties such as the polarity of an individual bond to sulphur are probably better represented by the larger basis at sulphur. An example of the latter is seen with our results for thiophen.[5a] The largest basis set gives results at sulphur and the adjacent

[18] H. C. Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 174.

TABLE 2

Orbital energies (eV) for the six-membered ring heterocycles

Benzenium cation	Pyridinium cation	*N*-Methyl-pyridinium cation	Pyrylium cation
a_1	a_1	a'	a_1
−314·9	−435·9	−436·2	−571·9
−314·8	−319·0	−318·8	−317·8
−314·0	−317·7	−318·7	−315·6
−313·2	−317·1	−317·5	−314·6
−36·68	−43·39	−317·0	−49·05
−35·11	−37·91	−317·0	−37·91
−29·54	−31·44	−316·7	−31·20
−26·23	−28·24	−43·80	−28·13
−24·01	−25·45	−38·12	−24·72
−22·85	−24·60	−36·38	−24·47
−20·08	−21·62	−33·84	−20·73
(+9·29)	(+1·63)	−31·41	(+2·74)
b_2	b_2	−30·42	b_2
−314·9	−319·0	−26·97	−317·8
−313·2	−317·1	−26·33	−314·6
−33·33	−36·44	−24·91	−36·58
−29·08	−31·26	−24·34	−31·81
−24·01	−26·25	−24·11	−26·52
−22·72	−24·18	−22·14	−24·08
−19·91	−21·72	−21·57	−21·61
(+10·49)	(+5·58)	−21·48	(+5·88)
b_1	b_1	(+3·32)	b_1
−23·23	−23·93	a''	−25·85
−18·41	−19·16	−24·91	−19·29
(−5·29)	(−5·32)	−21·61	(−5·07)
a_2	a_2	−18·66	a_2
−16·13	−17·84	−17·72	−17·44
(−1·40)	(−3·79)	(−5·23)	(−2·88)

Thiopyrylium cation		Phosphorin	
sp Basis	*spd* + 3*s*′ Basis	*sp* Basis	*spd* + 3*s*′ Basis
a_1	a_1	a_1	a_1
−2502	−2504	−2164	−2167
−315·4	−315·2	−307·3	−307·2
−314·9	−314·6	−307·2	−307·0
−314·3	−314·0	−306·4	−306·4
−246·3	−246·6	−195·6	−197·2
−188·6	−189·1	−143·3	−144·3
−39·25	−38·69	−31·02	−30·72
−35·74	−35·33	−26·56	−26·22
−29·79	−29·59	−21·65	−21·40
−26·40	−26·10	−19·44	−19·21
−24·11	−23·96	−17·10	−16·96
−22·27	−27·08	−15·08	−14·89
−19·37	−19·53	−9·92	−10·24
(+4·14)	(+3·58)	(+12·99)	
b_2	b_2	b_2	b_2
−315·4	−315·2	−307·3	−307·2
−314·3	−314·1	−306·4	−306·4
−188·7	−189·2	−143·4	−144·4
−35·09	−34·81	−27·85	−27·68
−29·75	−29·59	−22·34	−22·23
−24·60	−24·42	−16·91	−16·74
−23·54	−23·28	−16·52	−16·36
−20·38	−20·28	−12·87	−12·89
(+3·09)	(+1·59)	(+11·02)	
b_1	b_1	b_1	b_1
−188·6	−189·1	−143·3	−144·3
−21·72	−21·38	−14·25	−14·02
−17·79	−17·47	−9·23	−9·04
(−5·35)	(−5·02)	(+2·57)	
a_2	a_2	a_2	a_2
−17·12	−16·85	−10·30	−10·09
(−2·66)	(−2·76)	(+4·14)	

carbon atoms very similar to those of a much larger basis set calculation.[14] Thus if we wish to consider the polarity around the sulphur atom, we would wish to obtain results parallel to those of this larger calculation, and hence use the *spd* + 3*s*′ data for the population analysis. The effects further away from the sulphur atom can be deduced from the effects at sulphur, namely that an increase in basis set on the carbon and hydrogen atoms would probably reduce the charge separations on these CH bonds by a small amount. This would then restore the wave function to a balanced system and one in which the dipole moment would be well represented. We note here that the dipole moment of phosphorin is better represented by the *sp* basis result than the larger basis one (below). The orbital energies are largely unaffected by the basis set changes.

Molecular Orbital Energies

(a) *Comparison with Earlier Work.*[9,10]—The total energy for the benzenium cation (Table 1) lies between that of an earlier single ζ (−228·25309 a.u.) and double ζ (−230·67543 a.u.) calculation,[9] which in view of the

TABLE 3

Population analyses for the six-membered rings

Pyrylium cation	O(1)	C(2), C(6)	C(3), C(5)	C(4)	
$1s + 2s$	3·7471	3·0330	3·0523	3·0924	
sp_σ	3·0777	1·8869	2·0906	2·1890	
$2p_\pi$	1·6120	0·8311	0·9889	0·7479	
Total	8·4368	5·7510	6·1339	6·0292	
	H(2), H(6)	H(3), H(5)	H(4)		
$1s$	0·7368	0·7663	0·7594		
Thiopyrylium cation					
sp Basis	S(1)	C(2), C(6)	C(3), C(5)	C(4)	
$1s + 2s + 3s$	5·7293	3·1260	3·0510	3·0764	
$(2p + 3p)_\sigma$	6·3483	2·1351	2·1041	2·1785	
$(2p + 3p)_\pi$	3·4989	0·8942	0·9592	0·7979	
Total	15·7566	6·1653	6·1143	6·0528	
	H(2), H(6)	H(3), H(5)	H(4)		
$1s$	0·7469	0·7742	0·7689		
spd + 3*s*′ Basis	S(1)	C(2), C(6)	C(3), C(5)	C(4)	
$1s + 2s + 3s'$	5·3603	3·1004	3·0531	3·0736	
$(2p + 3p)_\sigma$	6·3517	2·0904	2·1095	2·1704	
$(2p + 3p)_\pi$	3·4741	0·8871	0·9468	0·8135	
$3d = 3s$ [a,b]	0·5313				
Total	15·7174	6·0778	6·1094	6·0575	
	H(2), H(6)	H(3), H(5)	H(4)		
$1s$	0·7598	0·7787	0·7735		
	$3s'$	$3d_\sigma$	$3d_\pi$		
S_1	0·3561	0·1306	0·0446		
Benzenium cation	C(1)	C(2), C(6)	C(3), C(5)	C(4)	
$1s + 2s$	3·0568	2·9923	3·0455	3·1047	
$2p_\sigma$	2·1244	2·1776	2·0751	2·2134	
$2p_\pi$	1·1826	0·7312	1·0266	0·6891	
Total	6·3637	5·9989	6·1472	6·0073	
	H(1), H(1′)	H(2), H(6)	H(3), H(5)	H(4)	
$1s$	0·7182	0·7746	0·7913	0·7683	
Pyridinium cation	N(1)	C(2), C(6)	C(3), C(5)	C(4)	
$1s + 2s$	3·3982	3·0686	0·0643	3·0869	
$2p_\sigma$	2·5202	2·0594	2·1615	2·2415	
$2p_\pi$	1·4483	0·8726	0·9945	0·8175	
Total	7·3666	6·0006	6·2203	6·1459	
	H(2), H(6)	H(3), H(5)	H(4)	H(1)	
$1s$	0·6912	0·7065	0·6977	0·5550	
N-Methylpyridinium cation [c]					
$1s + 2s$	3·3552	3·0635	3·0639	3·0850	3·2267
$2p_\sigma$	2·4592	2·0447	2·1644	2·2366	2·0069
$2p_\pi$	1·4303	0·8843	0·9893	0·8293	1·2414
Total	7·2446	5·9926	6·1277	6·1509	6·4750
	H(2), H(6)	H(3), H(5)	H(4)	$(\mathrm{H_i})_{\mathrm{ip}}$	$(\mathrm{H_i})_{\mathrm{oop}}$ ±
$1s$	0·6984	0·7081	0·7009	0·7369	0·7289

TABLE 3 (*Continued*)

Phosphorin				
sp Basis	P	C(2), C(6)	C(3), C(5)	C(4)
$1s + 2s + 3s$	5·6098	3·1410	3·0521	3·0473
$(2p + 3p)_\sigma$	6·0337	2·1849	2·1071	2·1064
$(2p + 3p)_\pi$	3·0287	1·0012	0·9846	0·9998
Total	14·6722	6·3271	6·1438	6·1539
	H(2), H(6)	H(3), H(5)	H(4)	
$1s$	0·8445	0·8487	0·8463	
$spd + 3s'$ Basis	P	C(2), C(6)	C(3), C(5)	C(4)
$1s + 2s + 3s$	5·3654	3·0868	3·0536	3·0451
$(2p + 3p)_\sigma$	6·0725	2·1231	2·1095	2·0994
$(2p + 3p)_\pi$	3·0027	0·9908	0·9739	1·0091
$3d + 3s'$ [a,d]	0·4725			
Total	14·9131	6·2008	6·1370	6·1536
	H(2), H(5)	H(3), H(5)	H(4)	
$1s$	0·8525	0·8575	0·8497	
	$3s'$	$3d_\sigma$	$3d_\pi$	
P	0·2552	0·1581	0·0588	

[a] The molecule lies in the *xz* plane with *z*-axis a symmetry axis. [b] Component as follows: $3s'$ 0·3568; $3d_{xz}{}^{\sigma}$ 0·0900; $3d_{x^2-z^2}{}^{\sigma}$ 0·0133; $3d_{y^2}{}^{\sigma}$ 0·0266; $3d_{xy}{}^{\pi}$ 0·0284; $3d_{yz}{}^{\pi}$ 0·0161. [c] Populations at C(2) and C(6), C(3) and C(5), H(2) and H(6), and H(3) and H(5) are virtually identical, and differ only in the orientation of the *N*-methyl group. Average values for these positions are recorded. [d] Components as follows: $3s'$ 0·2552; $3d_{xy}{}^{\sigma}$ 0·115; $3d_{x^2-z^2}{}^{\sigma}$ 0·0157; $3d_{y^2}{}^{\sigma}$ 0·0313; $3d_{gz}{}^{\pi}$ 0·0300; $3d_{yz}{}^{\pi}$ 0·0289.

single ζ nature of the present work is in the range expected. For phosphorin the results are some 6·25 a.u. *lower* than previous work [10] where a double ζ basis was used for the valency shell orbitals. In consequence the use of Koopmans theorem improves the agreement with experimental IPs [10] considerably.

(b) *Comparison of the Cation Series* (1a—e) *with Benzene* (1h).—Although the molecular symmetry in (1a—e) is C_{2v} rather than D_{6h} in benzene, there is a considerable similarity in the form of the molecular orbitals, and their groupings. A correlation diagram linking orbitals of similar type shows few cross-overs (Figure 1); thus even in the cations, the perturbation of the benzene energy levels is comparatively small, as in the azines,[4b] and a similar discussion can be given. For example, the splitting of the $3e_{1u}$, $2e_{2g}$, and $3e_{2g}$ benzene levels depends upon whether the X group is in a nodal position ($e_{1u\text{B}}$, $e_{2g\text{B}}$, or $e_{1g\text{B}}$) or not ($e_{1u\text{A}}$, $e_{2g\text{A}}$, or $e_{1g\text{A}}$) using the terminology of ref. 4*b* (*e.g.* 9—13). The remaining factor in the degree of splitting is the free atom orbital energy [11] of X for which relevant values are: $2s_\text{C}$ 19·20; $2p_\text{C}$ 11·79; $3s_\text{S}$ 23·94; $3p_\text{S}$ 11·90; $2s_\text{N}$ 25·72; $2p_\text{N}$ 15·44; $2s_\text{O}$ 33·86; $2p_\text{O}$ 17·20; $3s_\text{P}$ 18·95; $3p_\text{P}$ 10·66 eV respectively. These values reflect the electronegativities of the elements (C 2·5; P 2·2; N 3·0; O 3·5; S 2·5) and we have noted previously that the $-CH_2-$ group appears to be more electronegative than $-CH=$ from the $1s_\text{C}$ binding energies of conjugated olefins.[19]

(c) *Photoelectron Spectrum of Phosphorin.*—The experimental spectrum [10] shows IPs at 9·2, 9·8, 10·0, 11·5, and 12·1 eV with further broad bands centred on 13·1 and 14·5 eV and a weak band at 15·3 eV. The assignment of the first IP to ionisation from $3b_1$ has been supported by an earlier non-empirical calculation,[10] arguments based upon atomic ionisation energies,[10] and the effect of substituents [20] together with CNDO/2 calculations.[21] The present work bears out this conclusion. The order of the second, third, and fourth IPs, the first pair of which is too close to be resolved, has been more controversial; the CNDO/2 results, which the authors [21] did not accept, give the IP order $3b_1 < 13a_1 < 8b_2 < 1a_2$; the earlier non-empirical calculation and our (*spd* + 3*s*) basis set give the order $3b_1 < 1a_2 < 13a_1 < 8b_2$. Our most balanced (*sp*) basis set, yields the order $3b_1 < 13a_1 < 1a_2 < 8b_2$ which we believe is correct, and hence agree with Schweig's assignment.[20] We have repeated his CNDO/2 calculation and note that whilst it is possible to obtain a reasonable correlation with the eigenvalues up to the IP at 13·1 eV, thereafter the CNDO/2 calculation fails to give any account of the relative intensities of the lines at 13·1, 14·5, and 15·3 eV. Of course the LCGO (*sp* basis) and CNDO/2 orbital ordering is different and both cannot be correct at the same time. If 1, 3, and 1 IPs are assigned to these bands at 13·1, 14·5, and 15·3 respectively, which is not unreasonable on an intensity basis, the *sp* basis correlation line (assuming Koopmans' theorem) is then given by $\text{IP}_\text{obs} = 0{\cdot}62\ \text{IP}_\text{calc} + 3{\cdot}55$ eV; this is very similar to correlation lines of earlier studies[5c,6] with compounds containing second row elements. The calculation of ref. 10 gives a similar slope but a much

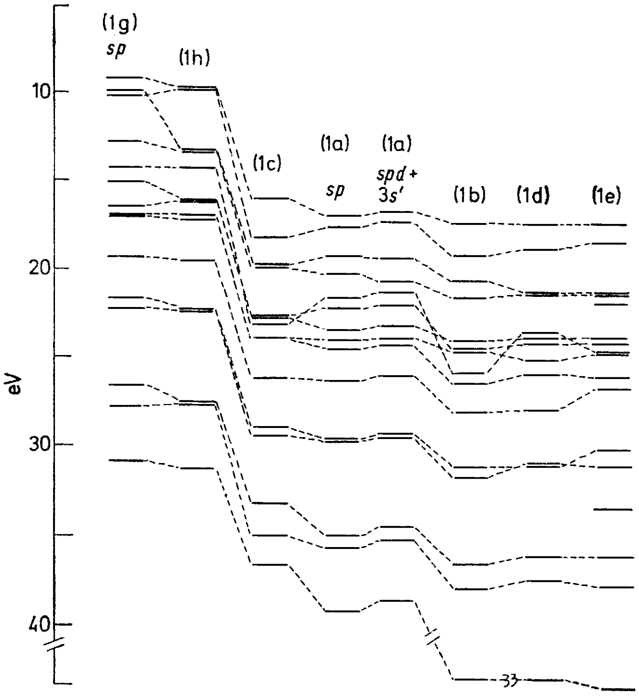

FIGURE 1 Energy correlation diagram for molecules (1a—e, g, and h)

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[20] (*a*) H. Schweig, W. Schafer, and K. Dimroth, *Angew. Chem. Internat. Edn.*, 1972, **11**, 631; (*b*) W. Schafer, A. Schweig, F. Bickelhaust, and H. Vermear, *ibid.*, p. 924; (*c*) H. Mase, A. Schweig, H. Hahn, and J. Radloff, *Tetrahedron*, 1973, **29**, 475.

[21] (*a*) H. Oehling and A. Schweig, *Tetrahedron Letters*, 1970, 4941; (*b*) H. Oehling, W. Schafer, and A. Schweig, *Angew. Chem. Internat. Edn.*, 1971, **10**, 656.

larger intercept of 5·1 eV; this is expected since the basis set used [22] normally gives IPs substantially lower than experiment for conjugated compounds,[23] a characteristic that is the reverse of most non-empirical calculations and is a sign of an inadequate basis set.

(d) *Chemical Consequences of Orbital Ordering*.—One aspect of phosphorin chemistry and the higher members of series (1; X = As, Sb, or Bi), which contrasts strongly with that of pyridine, is the ready Diels–Alder 1,4-addition which occurs in the former series, but not in the latter. Thus phosphorin adds across 1,4-positions, arynes [24] and activated acetylenes,[25] and singlet oxygen,[26] whereas pyridine does not. This is a direct consequence of the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals of (1; X = P, As, Sb, and Bi) being of b_1 symmetry, and of the forms (16) and (17) respectively; they are thus able to mix effectively with the bonding and antibonding orbitals of the incoming reagent. In pyridine (and the pyrylium cation) the highest occupied orbital is $1a_2$ and the lowest unoccupied $3b_1$. Although it is not surprising that these species do not undergo the Diels–Alder reaction, the ready singlet excitation of the 2,4,6-trimethylpyrylium cation to an oxoniabenzvalene (18) [27] is consistent with the LUMO being of type (17), and the initial cyclisation reaction leading to C(2)–C(6) closure. Strictly, we need to confirm that the excitation energy $2b_1 \longrightarrow 3b_1$ in this instance is low but the eigenvalue for the $3b_1$ orbital is so much lowered relative to $2a_2$, *etc.*, that it seems certain to be the case. A similar approach explains the triplet excited thiopyrylium addition of (triplet) oxygen to the 2,5-positions; [28] here the HOMO and LUMO (1a) are both of a_2 symmetry.

Electronic Charge Distribution

Phosphorin.—One of the most sensitive tests of overall electronic charge distribution is the electric dipole moment; however, this is only unique in value for neutral molecules, varying with the position of measurement in ions. For phosphorin, the experimental dipole moment magnitude 1·54 ± 0·02 D has been obtained by microwave spectroscopy.[16] The calculated moments, *sp* basis 1·87 and *spd* basis 0·99 D, lie to each side showing the sensitivity to the basis set. The agreement with the former figure is acceptable, and since the absolute error necessary to change the sign is unreasonable for a molecular calculation of this size,[4a] we conclude that the sign with negative end towards phosphorus is clearly established.

It is important to note however, that in contrast to the nitrogen of pyridine,[4a] the phosphorus atom is slightly positively charged in the Mulliken population analysis. This is readily understood in terms of the electronegativities of the elements: H 2·2; C 2·5; N 3·0; P 2·2. It is is well established [4a, 29] that there is no simple relationship between Mulliken population analyses and molecular dipole moments in molecules with lone pair (LP) electrons Thus in the case of phosphorin the overall dipole moment is *largely* made up from contribution $LP + C_{\gamma}H_{\gamma} + 2C_{\alpha}P$ where $C_{\gamma}H_{\gamma}$ and $C_{\alpha}P$ represents that bond contribution summed along the *z*-axis. With the present system of delocalised molecular orbitals, it is not easy to evaluate the individual terms in this expression, but for phosphine (which has a rather small $\widehat{HPH}$ angle of 93·7°) we found [30] the lone pair moment to be 2·8 D; * this is nearly balanced by the PH moments (−1·2 D) in the opposite direction giving an overall small moment 0·80 D (experimental [31] 0·578 D). For phosphorin, the orbital $13a_1$, contains almost all the $(3p_z)_P$ population (1·1356, total 1·2978), but has a high $3s_P$ component (0·4109) and thus corresponds to $sp^{2\cdot76}$ hybridisation. This orbital which is largely a lone pair one contributes 0·4 D to the molecular dipole moment, a much lower value than that in phosphine owing to (a) the lower proportion of $3p_P$ character, itself a consequence of the increase in angle ($\widehat{CPC}$ 102·9°), and (b) the small contributions of the CP character in the reverse direction (0·46 e lie at other centres). Thus in phosphorin, much of the dipole moment probably arises from the $C^{\delta-}$–$H^{\delta+}$ polarisation, rather than the lone pair moment. It is interesting to note that contributions of the π-electron polarisation to the dipole moment are small, as also indicated by the population analysis. This is similar to the LCGO calculations on pyridine,[4a, 32] and shows that the large π-charge separations of some semi-empirical methods, *e.g.* CNDO/2 [21a] are unreasonable.

Cations (1a—e).—The population analyses for these species show a number of unexpected features; for example, the oxygen atom of the pyrylium cation is apparently negatively charged (−0·4368). Thus it is appropriate to establish (a) the norm for populations in neutral hydrocarbons (here C_2H_4 and C_6H_6); then (b) to consider the effect of molecular positive charge on a small hydrocarbon system, the allyl carbonium ion. Finally we proceed *via* the benzenium cation to the heterocycles.

Non-empirical calculations using either Slater or

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* Using the present gaussian set and the *spd* basis we obtained a total energy for phosphine of −341·8773 a.u., a binding energy of 8·79 eV, and dipole moment of 0·800 D. A comparison of these figures with experiment and with other calculations is given in ref. 30. The valency shell orbitals in PH_3 are: $4a$ (PH); $5a$ (LP); $2e$ (PH). There is very little sp_P character in $4a$ and little PH in $5a$ [total populations of $(3p_z)_P$ and $3s_P$ are 1·5173 and 1·6173 respectively, while in $5a$ only they are 1·4549 and 0·3468 respectively and thus the lone pair orbital is largely of *p* character ($s^{0\cdot35}p^{1\cdot45} \equiv sp^{4\cdot2}$ hybridisation)], hence it is possible to evaluate the individual LP and PH moments by summation over the separate orbitals, and we obtained μ_{LP} 2·8, μ_{PH} −1·2 D (negative end towards H).

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gaussian type orbitals normally lead to population analyses that imply a $C^{\delta-}$–$H^{\delta+}$ bond dipole,[*] with the values of $\pm\delta$ varying slightly with the basis set. Thus for the present minimal basis set for ethylene we obtain $\delta = \pm 0{\cdot}1154$. We have shown how reproducible these population dipoles are in earlier work.[5a] We thus adopt this value of δ as being a norm for CH bonds, and use the differing values of δ in the ions (1a—e) to apportion the positive charge to the molecular centres. Thus for the allyl carbonium ion, the average CH populations have δ 0·2369, indicating that *ca.* 0·6075 e are absorbed by the hydrogen atoms. Since the terminal carbon atoms might have been expected to have δ —0·2308 rather than —0·0160 obtained, we conclude that they are positively charged by 0·2148 e with the central carbon atom very slightly negative (0·0371 e). This slight alternating polarisation has often been observed in SCF calculations, and probably indicates that an element of stabilisation is achieved by electrostatic attraction in this way.[35] It is equivalent in resonance theory to arguing that the additional resonance form (13) stabilises the cation, but that the main canonical form is (14).

TABLE 4

Contributions to the molecular charge by centres

	X	C(2), C(6)	C(3), C(5)	C(4)	H(2), H(6)	H(3), H(5)	H(4)
$C_6H_7^+$ (X = CH_2	+0·2008 [a] (+0·2000) [b]	+0·1248 (+0·1165)	−0·0318	+0·1081	+0·1100	+0·0933	+0·1163
$C_5H_5S^+$ (X = S)	+0·2551 (+0·2826)	+0·0513 (+0·0376)	+0·0060	+0·0579	+0·1248	+0·1059	+0·1111
$C_5H_5O^+$ (X = O)	+0·0752 (−0·4368)	+0·1084 (+0·3644)	−0·0185	+0·0875	+0·1478	+0·1183	+0·1252
$C_5H_5NH^+$ (X = NH)	+0·2284 [c] (+0·0784) [d]	+0·0398 (+0·1148)	−0·1049	−0·0305	+0·1934	+0·1792	+0·1872

[a] H, +0·1557; C, −0·0307. [b] H, +0·0899; C, +0·0202. [c] H, +0·1152; N, −0·0368. [d] H, +0·4450; N, −0·3666.

In the benzenium cation (1c), the CH_2 group is positively charged overall by 0·2000 e, and it seems that this is largely carried by the hydrogen atoms; using the the value of δ 0·1154 for the neutral ethylene molecule, we assign the charges to the ring atoms as follows: H(2) +0·1100; H(3) +0·0933; H(4) +0·1163; C(2) +0·1165; C(3) —0·0318; (C4) +0·1081. These figures are very similar to those calculated for the allyl carbonium ion. It thus seems that the present results support the contributions of the resonance structures (6 and 7; X = CH_2) in the ratio 2 : 1, *i.e.* on a statistical basis.

The total populations of the hydrogen atoms in the heterocyclic cations (1a, b, and d) are very similar to those of the above. Those for the ring atoms of (1a—c) follow the expected order at the heteroatoms O > C > S; the ring carbon atoms show the same trends C(3) > C(4) ~ C(2) except that in the pyrylium cation C(2) is lowered further. The pyridinium cation shows unexpected differences, with the nitrogen and β-carbon atoms being more heavily (negatively) charged and most of the molecular positive charge being absorbed by the hydrogen atoms. We have estimated the extent of the atomic contributions to absorption of the positive charge (Table 4) by using the charge separations at the CH bonds as above but clearly the electronegativity of the heteroatom needs to be taken into account in assessing the polarity of the $C_\alpha X$ bonds (X = S and O) in particular; it is difficult to obtain satisfactory reference figures here, but we have utilised our data[2a,30] on the neutral species (15; X = CH_2, S, NH, and O). For example in furan, the C_α–O bond is polarised $C_\alpha^{\delta+}$–$O^{\delta-}$, with δ 0·2506; thus the additional charge on the C_α atom in (1b) must be the extent of localisation of the positive charge at C_α (+0·1084). In this way we assign the overall charges shown (Table 4) with the figures for C_α and X before taking into account the polarisation of the C_α–X bond (or the NH bond) in parentheses. The derivation of these figures is not rigorous, but by the standardised procedure probably indicates relative values realistically. We see that in (1a—c) the extent of positive charge absorption is largely even in all hydrogen atoms (+0·12). For the carbon atoms, C_β is effectively neutral, C_γ is *ca.* +0·08, and C_α +0·08. The positive charges (S > O) on the ring heteroatoms in (1a and b) are reasonable. The σ populations at carbon are largely unchanged over those of the corresponding neutral molecules such as (15). For these molecules the overall charge distributions in Table 3 run parallel to the π-population data (Table 3). In contrast, in the pyridinium cation (1d), the positive charge arises in the σ-system, it is relayed through the system to the hydrogen atoms more effectively[*] than in (1a and b) where it is necessary to have a $\pi \longrightarrow \sigma$ exchange procedure. Similarly the uncharged π-system is

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[*] In organic chemistry texts widely used in teaching[33] it is maintained that the C–H bond dipole is polarised in the reverse sense, and it has been noted that this requires an exception to be made to the usual arguments based upon electronegativity. Certainly as far as first and second row elements (X) are concerned, non-empirical calculations appear to support the Pauling electronegativity scale for X–Y bonds *including* CH. The evidence on which the $C^{\delta+}$–$H^{\delta-}$ conclusion is based appears to arise from microwave studies of the effect on dipole moments of CD relative to CH. These data show that D is more electropositive than H, but do not give the polarisation of either relative to carbon.[34]

[*] It is interesting to note that Clementi's study[36] of the $2A_2$ radical cation of pyridine, where a π-electron was ionised, also showed that the major rearrangement of charge was in the σ- rather than the π-system. Furthermore that the populations at hydrogen atoms absorbed all the positive charge (Table 7 of ref. 36), although there were minor changes in the ring atoms at the same time.

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[35] L. Salem, ' The Orbital Theory of Congugated Systems,' Benjamin, New York, 1966, p. 64.

[36] E. Clementi, *J. Chem. Phys.*, 1967, **47**, 4485.

capable of attenuating the σ-charge separations more easily, and thus achieves a substantial π-positive charge at C_α and C_γ but with negligible effect at the C_β atoms. Overall the total populations of the heteroatoms in (1a, b, and d) are remarkably similar to that in the neutral five-membered rings (13; X = O) 8·5120; (13; X = S) 15·9790; (13; X = NH) 7·4799.

It is clear that interpretation of the electronic structures of these cations by π-electron canonical forms (5)—(7) is a serious error. Thus in (1a and b), forms (5)—(7) only account for *ca.* 0·4 e; for (1b), (6) contributes rather more than its statistical value and (5) rather less, while for (1a) the contribution of (5) is *ca.* 60% to this partial total of 0·4 e. All the positive charge in (1d) lies in the σ-system, but in so far as (6) and (7) indicate the polarisation of the π-system to accommodate this, the contributions of (6) and (7) are 26 and 19% respectively.

Aromatic Character

We have noted earlier [4a] that if a π-electron set is to be heavily delocalised, then the set should behave as a group and not separate out into individual pairs. Thus the average position of the π-electrons, evaluated quantum mechanically over the electronic wave-function, should be similar for all members of the set. Of course in benzene and some other molecules this is automatically the case from symmetry considerations above. We have recorded data for the five-membered ring heterocycles (13; X = NH, O, S, and PH) previously [4a] and chose the $C_\beta C_\beta$ bond as reference point, owing to the major geometry variations occurring in the vicinity of X. It is convenient to apply the same procedure to the present conjugated systems (Table 5), retaining the same reference axis.

In the following discussion the $2p$ π-orbitals of sulphur and phosphorus are ignored since they play no significant part in the molecular bonding; we also note that the data of Table 5 are largely unaffected by the basis sets on S and P. The average position of the $1a_2$ orbital, which is nodal at the heteroatom is largely constant for all the six-membered rings studied (1a, b, d, f, and g) and its position is comparatively close to the midpoint of the $C_\alpha C_\beta$ bond; in contrast the same orbital in the five-membered rings (15) is significantly nearer the C_α position.[4a] Thus in the latter instances it is more suitably placed for Diels–Alder 2,5-addition (see below). The position of the inner valency shell b_1 orbital [π_1 in (1b, d, and f), π_2 in (1a and g)] is close in the cations [1a, b, d] to that of the corresponding five-membered ring heterocycles (13),[4a] and much further away in the neutral molecules (1f and g). This shows how the π-electrons are heavily polarised towards the heteroatom by the positive charge [*cf.* canonical forms (5) and (6) on a π-resonance basis]. We adopt our earlier proposal for 6π-electron systems, that the degree to which the system separates into a quartet and a pair gives a measure of the degree of classical character, and the closeness of the set as a measure of aromaticity. This procedure is directly applicable to the cations (1a and b) since here the heteroatom [*cf.* (6) and (7)] can be regarded as providing 2π-electrons; for (1d), it refers to a similar structure consisting of penta-1,3-dienylium cation and a pyrrole type nitrogen atom. The separation of the inner pair of π-electrons from the average of the quartet is then: benzene (0·0), pyridine (0·154), thiophen (0·340), thiopyrylium cation (0·420), phosphorin (0·583), pyrrole (0·680), furan (0·84), phosphole (0·82), pyrylium cation (0·97), and pyridinium cation (1·04). The non-planar character of phospholes [5a] and the ready nucleophilic substitution in the pyrylium and pyridinium cations fit with this picture and the lower aromaticity of (1b) than (1a) claimed from i.r. measurements [37] is produced.

TABLE 5

Average position of the π-electrons from the $C_\beta C_\beta$ axis [a]

	Pyridine (Å)	Phosphorin (*sp*) (Å)	Phosphorin (*spd* + 3*s*′) (Å)	Pyridinium cation (Å)
π_1 [b]	0·804	2·481	2·480	1·510
π_2 [b]	0·600	0·385	0·377	0·189
π_3 [b]	0·699	1·220	1·171	0·741
π_4 [b]		0·7167	0·748	
Average position	0·701	0·763	0·765	0·813
Position range	0·204	0·835	0·794	0·769
C_α Co-ordinate	1·392	1·396	1·396	1·392
X Co-ordinate	2·071	2·480	2·480	2·071

	Pyrylium cation (Å)	Thiopyrylium cation (*sp*) (Å)	Thiopyrylium cation (*spd* + 3*s*′) (Å)
π_1 [b]	1·738	2·421	2·421
π_2 [b]	0·012	1·205	1·164
π_3 [b]	0·754	0·800	0·783
π_4 [b]		0·778	0·815
Average position	0·835	0·928	0·921
Position range	1·726	0·427	0·381
C_α Co-ordinate	1·400	1·392	1·392
X Co-ordinate	2·036	2·421	2·421

[a] Co-ordinates of $C_\beta = 0$ along the C_2 symmetry axis.
[b] π_1, π_2, π_3 (and π_4 where appropriate) in decreasing order of binding energy as in Table 8 of ref. 4*a* and not as stated there.

Electron Distribution and Proton Chemical Shifts

In this paper we have confirmed our earlier view [5a] that the $3d$ orbitals do not significantly effect the bonding in the thiopyrylium cation (or in phosphorin). This view has been disputed,[38] on the basis of the unusual proton chemical shifts in the series (1a, b, and e) (or strictly the *N*-ethyl derivative). The experimental figures seem to be largely independent of solvent and temperature and earlier figures [39] are reproduced in Table 6. The notable feature is the relative position of H(2) in the thiopyrylium and pyrylium cations, where the expected deshielding of oxygen relative to sulphur is absent. This, and the degeneracy of the H(3)/H(4) in the former (1a) is claimed [38] to arise from electron withdrawal from C(3) by means of $3d$ orbital participation (20).

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[37] Z. Yoshida, H. Suzimoto, and S. Yoneda, *Tetrahedron*, 1974, **30**, 2099; 1972, **28**, 5893.

[38] S. Yoneda, T. Sugimoto, and Z. Yoshida, *Tetrahedron*, 1973, **29**, 2009.

[39] T. J. Batterham, ' N.M.R. Spectra of Simple Heterocycles,' Wiley, New York, 1973, pp. 57, 388, 454.

TABLE 6

Proton chemical shifts and calculated electric field components

	2-H		3-H		4-H	
	δ_{Calc}	δ_{Obs}	δ_{Calc}	δ_{Obs}	δ_{Calc}	δ_{Obs}
Benzenium cation	10·20	9·58 [a]	8·66	8·22 [a]	10·34	9·42 [b]
Pyrylium cation	12·10	9·59 [b]	9·35	8·40 [b]	10·51	9·20 [b]
Thiopyrylium cation (*sp*)	9·37	10·13	9·47	8·97 [b]	9·97	9·00 [b]
Thiopyrylium cation (*spd* + 3*s*′)	10·24	10·13	9·57	8·97	9·90	9·00
N-Methyl-pyridinium cation	9·43	8·77	8·79	8·04 [b]	11·08	8·53 [b]

[a] G. A. Olah, R. H. Scholesberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, 1972, **94**, 2034. [b] Ref. 39.

We consider the proton resonance below, but first note that extended Hückel MO calculations (EHMO) were cited [38] as evidence that 3*d* orbital participation occurs, and that electron withdrawal from C_β is substantial by that mechanism. First we note that the population at C_β is largely unchanged (for *sp* and *spd* + 3*s*′ bases) in the present *non-empirical* calculations; secondly that the populations in the EHMO calculations are unrealistic in view of the electronegativity of H 2·2; C 2·5; S 2·5 and general principles. Thus the principal charges in the overall cation from the EHMO calculations are: (C2), C(6) +0·93; C(3), C(5) +0·26; C(4) +0·33; and S −2·00 with hydrogen varying from +0·03 to +0·08. We conclude that these are physically unrealistic, particularly at C(2), C(6), and S, and that the 3*d* orbital participation which doubles the negative charge on sulphur is an artefact arising from the parametrisation.

The accurate interpretation of chemical shifts at a non-empirical level is not yet possible, owing to the necessity of evaluation of the paramagnetic term to the shielding constant over an (infinite) series of excited states. Even under semiempirical procedures it is necessary to invoke an average excitation energy approach to this latter term in order to obtain correlations in chemical shifts for heterocycles, and the results meet with mixed success.[28] It has been shown, however, that intramolecular electric fields may offer an explanation of much of the relative shielding in the 2,3,4,5,6-pentamethylbenzenium cation,[40,*] and the pyridinium cation.[41] Here we attempt a similar analysis to determine whether the resultant relative shieldings parallel the observed ones, and if not to see whether the differences can be correlated with the aromaticity differences found above.

We evaluate the effect of the charge distribution given by the population analysis in two stages;[42] the local spherical (proton) charge (Δρ) is given by the Lamb equation (2). The effect of remote charge q_i at distances r_i, making an angle θ_i with the CH bond axis is given by equation (3).

$$\Delta\sigma = \frac{e^2}{3mc^2a_0}\,\Delta\rho = 17{\cdot}7 \times 10^{-6}\,\Delta\rho \text{ p.p.m.} \qquad (2)$$

$$\Delta\sigma = 12{\cdot}5 \times 10^{-6}\sum_i \frac{q_i cos\theta_i}{r_i} - 17{\cdot}0 \times 10^{-6}\sum_i \frac{{q_i}^2}{{r_i}^4} \qquad (3)$$

Using the population analysis data for ethylene, and summation over all centres we find the charge distribution to be responsible for a shift ($\Delta\sigma_T$) of *ca.* −1·06 p.p.m., *i.e.* the resonance would be downfield of the experimental position (δ 5·28) if the bonds were neutral. Most of this effect arises from the difference between the contributions of directly bonded C and H in opposite directions. For the allyl carbonium ion similar calculations lead to total contributions ($\Delta\sigma_T$) of H(1), H(3) 5·14; H(2) +2·49 which lead to δ 11·47 [H(1)] and 8·83 [H(2)]. As expected the figures are only in qualitative agreement with experiment, with the internal shift of 2·6 p.p.m. being rather larger than that of substituted allyl carbonium ions.† Similar calculations for the

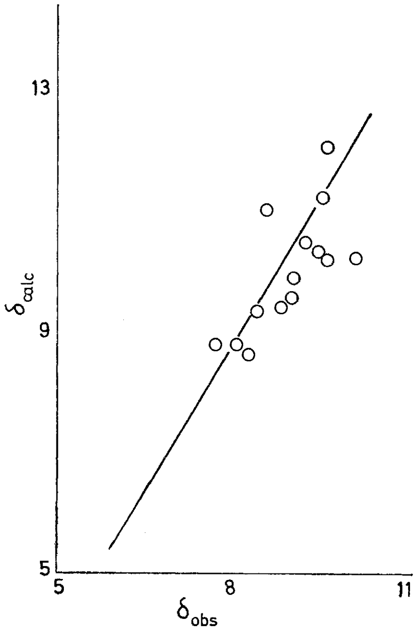

FIGURE 2 Experimental and calculated ^{1}H chemical shifts

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* In this work [40] the positive charge was arbitrarily assigned as +1/5 at C(2) to C(6), and the total deshielding shown to lead to a value of the constant *k* relating the shielding constant (σ) to electric field (E_z) by $\sigma = k\Delta E_z$, which was in agreement with that deduced theoretically.

† The position for the parent allyl carbonium ion, is more complex; in SbF_5,SO_2 it exhibits [43] a broad singlet at δ 9·64, [H(2)], and a doublet at 8·97 [H(1), H(3)]. The position of the terminal H(1) resonances are consistent with methyl substituted species, and H(1) and H(5) of pentadienylium cations,[44,45] while the central proton H(2) is substantially shifted from that of these methyl and pentadienyl species. The degeneracy of the terminal protons, known interconversion to cyclic species under the conditions,[44] and similarity of the H(2) shift to that of the cyclopropenylium cation [44] suggest that δ 9·64 includes a large contribution of cyclopropenium character; it is therefore anomalous and a better value is obtained from the substituted compounds [45] with δ 7·7, *i.e.* an internal chemical shift difference of δ 1·2 p.p.m.

[40] J. I. Musher, *J. Chem. Phys.*, 1962, **37**, 34.

[41] V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, 1964, **60**, 248; see also P. J. Black, R. D. Brown, and M. L. Heffernan, *Austral. J. Chem.*, 1967, **20**, 1305.

[42] L. M. Jackman and S. Sternhell, 'Nuclear Chemistry,' Pergamon, Oxford, 1969, 2nd edn.

[43] G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1964, **86**, 5682.

[44] T. S. Sorensen, *Canad. J. Chem.*, 1964, **42**, 2768; G. A. Olah, C. U. Pittman, and T. S. Sorensen, *J. Amer. Chem. Soc.*, 1966, **88**, 2331.

[45] N. C. Deno, H. G. Richey, N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, *J. Amer. Chem. Soc.*, 1963, **85**, 2991.

benzenium, pyrylium, *N*-methylpyridinium, and thiopyrylium cations lead to the results in Table 6 and Figure 2. Bearing in mind the nature of the procedure, based upon the population differences at each centre, the results are surprisingly good, and confirm the earlier view that intramolecular electric fields play a major part in the screening of charged molecules. However, the present results do not account for the shift to low field of the thiopyrylium relative to pyrylium cation resonances. We note, however, that if the former points are shifted upfield by *ca.* 1 p.p.m. then the data straddle the correlation line. This shift is about what we would expect from a substantial ring current, where for example the value of benzene is *ca.* 1·5 p.p.m. Our discussion above, on the degree of aromaticity based upon average positions of π-electrons, supports this specific effect upon the thiopyrylium cation relative to the other molecules under consideration. The observed shifts can thus still include a contribution from the magnetic anisotropy of the heteroatom, and yet still lead to the observed relative shifts. Although the effect of the 3*d* orbital calculation for (1a) leads to a specific shift of H(2) to lower field relative to the *sp* basis results, this largely arises from the smaller dipoles on the HCS system, and not from heavy contributions in the 3*d* orbitals as proposed elsewhere.[38]

Conclusions

The present calculations show a considerable similarity in the molecular orbital energies for the cations (1a—e) and the neutral molecules (1f—h). Nonetheless, the average positions of the π-electrons differ significantly in the series and only the thiopyrylium cation seems to be strongly aromatic by this criterion. This is supported by the calculations of the intramolecular electric fields and their contribution to the chemical shifts.

Most of the positive charge in the cations is absorbed by the protons, and this shows again the inadequacy of resonance structures based purely upon π-electron polarisation.

[4/2144 *Received*, 17*th October*, 1974]