Electronic Charge Distribution and Moments of Five- and Six-membered Heterocycles

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Using *ab initio* wave functions and the full operators, dipole and second moments are reported for a number of five- and six-membered ring heterocycles containing the elements nitrogen, oxygen, sulphur, and phosphorus. The agreement with experiment is satisfactory and a linear relationship $\mu_{\text{exptl.}} = 0{\cdot}952\mu_{\text{calc.}}$ is obtained with an average error of 0·29 D. With the exception of the quadrupole moments, the second moments are just outside the experimental error in the worst cases. Population analyses for the compounds are found to be additive in bond contributions, and this assists in the interpretation of the σ- and π-dipole moments. The difference in average position between the valency shell π-electrons has been related to aromatic character.

THE dipole moments of furan (0·67 D), pyrrole (1·80 D), and thiophen (0·53 D) have long been known,[1] but the direction of these moments has remained a controversial matter.[2-4] We have recently completed a series of non-empirical calculations of wave functions for most of the five- and six-membered heterocycles which contain varying numbers of nitrogen atoms with one oxygen, sulphur, or phosphorus atom. The total and molecular orbital energies of many of these molecules have been reported elsewhere.[5-8] We report here the molecular dipole moments obtained from these wave functions together with results of calculations of second moments. Although electron density at a point in space cannot be strictly equated with Mulliken populations,[9] it is often convenient to have a single parameter which indicates the overall character of an atom. We thus include a detailed analysis of the Mulliken populations and show that constant bond contributions occur.

It is important to state unequivocally at the outset that the adequacy of these calculations is determined by the geometry for the system being investigated. There is still comparatively little accurate data on simple heterocyclic species. It is clear that the azoles in the crystalline state, at least, are heavily hydrogen bonded;[10,11] since our calculations refer to a single molecule in isolation, there is no real substitute for a gas-phase structure determination by either microwave spectroscopy or electron diffraction. In the present work we have used microwave determined structures where possible; crystal structures have been used as a second choice, but even then it has been necessary to construct geometries for many of the molecules studied, and we have used known bond lengths in the series to achieve this.

METHODS

The primary differences between the present work and most previous calculations are as follows: (a) all electrons are included in the calculation; *i.e.* not only π-electrons or valency shell electrons; (b) the calculations are effectively at the Hartree–Fock limit;[10,12] (c) all integrals required by this theory have been explicitely evaluated without the introduction of empirical parameters or experimental data; and (d) the correct operator is used in calculation of the molecular property. This last point is of fundamental importance; in empirical theories it is common to use a point charge distribution for the dipole moment (with the addition of a lone pair moment in the VESCF method [13,14]), whereas for semi-empirical methods such as CNDO/2 and INDO [15] this is partially corrected by the addition of a hybrid moment to take account of the non-identity of nuclear and electronic charge positions at a centre carrying both $2s$ and $2p$ orbitals.[16] When results obtained by the latter technique are reinterpreted in terms of the full operator, the agreement between the calculated values (*e.g.* with CNDO/2) and experiment is variable and not always so good as before correction.[15] We have used one set of gaussian functions for each atomic orbital $1s_{\text{H}}$, $2s_{\text{N}}$, *etc.*[5,6] The exponents and contraction coefficients (weighting factors) were optimised for the corresponding atoms (' Best Atom ' bases) and are described in detail elsewhere,[5-8] but for $1s_{\text{M}}$, $2s_{\text{M}}$, $2p_{\text{M}}$ (M = C, N, or O), and $1s_{\text{H}}$ consist of 5, 2, 3, and 3 gaussian functions respectively. For the second row atoms the functions $1s_{\text{M}}$, $2s_{\text{M}}$, $3s_{\text{M}}$, $2p_{\text{M}}$, $3p_{\text{M}}$, and $3d_{\text{M}}$

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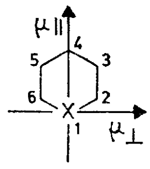
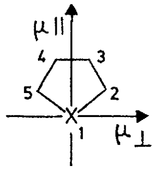
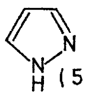
(M = S or P) consisted of 6, 2, 2, 4, 2, and 1 gaussians respectively. Six *d* orbital functions $(d_{x^2}, d_{y^2}, d_{z^2}, d_{xy}, d_{xz}$, and $d_{yz})$ were used for the compounds containing single second row atoms of sulphur or phosphorus; this is necessary in the linear combination of gaussian orbital (LCGO) procedures to preserve the three-fold symmetry of the calculations of the molecular integrals. These six functions were then contracted to the usual five *d* functions and another *s* function by standard procedures.[17] The wavefunctions were obtained using the computer programs IBMOL-4 and ATMOL-2 on IBM370/155 and IBM360/195 computers, and the first and second moments were obtained by use of the programs POPUL (a satellite program of IBMOL-4) and ATMOL-2, and POLYATOM-2 respectively. It has not yet been possible for us to perform σ–π separations for the dipole moments of molecules computed with the ATMOL-2 program.



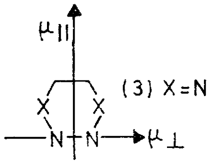
(1) X = N or P



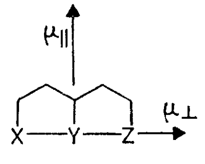
(2) X = NH, PH, O, or S



(5)



(3) X = N, or CH



(4) X, Y, Z = S, O, NH

The orientation of the molecules used in describing the results for the dipole moments (Tables 1 and 2) are as shown in (1)—(4). It is convenient to define two axes for the dipole moments, the parallel ($\mu_{\|}$) and perpendicular ($\mu_{\perp}$) as shown [(1)—(4)]. All the ring systems are orientated with their numbering anticlockwise; the sign of the dipole moment vector component is taken with the *negative* end in the *positive cartesian* direction as positive, and this leads to the usual experimental proposition that the dipole moments of furan and pyrrole, of opposite sign, are negative and positive respectively. The dipole moment operators can be evaluated at any set of cartesian axes through an arbitrary origin. However, the second moment is origin dependent and is conventionally evaluated at the centre of mass; this enables direct comparison with the microwave measurements of Flygare *et al.*[18–20]

In view of the importance traditionally placed upon the π-electron distribution in aromatic species, it is appropriate to consider two alternative dipole moment vector components, the μ_σ and μ_π components. It is apparent that separation of μ_σ and μ_π at a theoretical level involves an element of arbitrary character. Although the average position for the six π-electrons in pyrazole (for example) or the thirty σ-electrons can be readily calculated by summation of the components from each of the appropriate occupied orbitals, this is not the case with the nuclear component; thus the summations of the types $\Sigma z_N x_N$ cannot unequivocally be separated into a σ- and π-component. If the classical structure for pyrazole (5) is used, then the secondary nitrogen atom, tertiary nitrogen atom, and carbon atoms provide two, one, and one π-electrons respectively, so that the effective nuclear charges for the π-components are +2, +1, +1 respectively, while for the σ-system the nuclear charges are +5, +6, +5 respectively with +1 for hydrogen atoms. This system has been much used[21] and is also shown in Tables 1 and 2. The weakness is that (a) it refers to a hypothetical molecule [*e.g.* (5)] and (b) that the uncharged species (5) could still have homopolar σ- and π-dipole moments of opposing signs.[22]

RESULTS AND DISCUSSION

Dipole Moments. The Overall Position.—The average error between the experimental magnitudes and the values obtained by the LCGO calculations is 0·29 D, and the results obey the relationship $\mu_{\text{exptl.}} = 0{\cdot}952\ \mu_{\text{calc.}}$ If only the molecules where microwave-determined structures are considered, then the line slope moves to the other side of the theoretical correlation with $\mu_{\text{exptl.}} = 1{\cdot}14\ \mu_{\text{calc.}}$ with an average error of 0·05 D. In all cases, therefore, where gas-phase geometries have been used theory and experiment follow closely a linear relationship. Thus much of the scatter for the remaining molecules must be attributed to inadequate representations of the geometry; another factor is that our basis set is probably rather inflexible for highly polar groupings, such as NH bonds, and this contributes in the case of pyrrole and the azoles. Nonetheless it is clear that the agreement with experimental magnitudes is sufficiently good that we can regard the sign of the dipole moments in this series of compounds as finally settled. In the molecules with C_s symmetry the overall dipole moment vector could be in error in direction (*i.e.* $\mu_{\|} : \mu_{\perp}$ ratio), but probably not by a large amount. Experimentally there appears to be little information on the principal dipole moment vector components; various workers have recorded rotational constants A, B, and C for five-membered ring heterocycles, but the directions of the in-plane components μ_a and μ_b are not known for pyrazole,[23] imidazole,[24] 1,2,4-triazole,[25] or 1,2,4-oxadiazole.[24] Until analyses of these microwave spectra and those of the ^2H, ^{13}C, and ^{15}N labelled analogues are reported, we are unable to compare the theoretical orientations with experiment accurately. A survey of

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TABLE 1

Dipole moments (μ/D) and vector components in five-membered rings

Name	Experimental value	LCGO				
		Total μ	$\mu_\perp$	$\mu_\parallel$	μ_σ	μ_π
Pyrrole	1·80 [b]	2·01	+2·01	0·0	−0·53	+2·54
Pyrazole	2·21 [c]	2·85	+2·23	+1·77	+1·65 (−30·1°) [a]	+3·07 (+83·0°) [a]
Imidazole	3·8 [d]	4·41	+4·31	+0·96	+1·46 (+52·4°) [a]	+3·15 (+95·3°) [a]
1*H*-1,2,4-Triazole	3·20 [e]	3·56	+3·50	+0·65	1·14 (+54·0°) [a]	2·91 (+86·6°) [a]
1*H*-1,2,3-Triazole		4·50	+3·26	+3·10	2·79 (+81·7°) [a]	2·87 (+83·0°) [a]
2*H*-1,2,3-Triazole		−3·24	−3·26	0·0		
1*H*-1,2,3,4-Tetrazole	5·15 [f]	5·17	+4·72	+2·11	2·53 (+47·0°) [a]	2·92 (+82·5°) [a]
2*H*-1,2,3,4-Tetrazole	(2·30) [h]	2·54	+2·24	+1·22	1·57 (−25·8°) [a]	2·71 (+94·1°) [a]
Furan	0·67 [b]	−0·64	−0·64	0·0	−2·77	2·13
Thiophen (*sp* basis)	0·53 [b]	−1·25	−1·25	0·0	−3·22	1·97
(*sp* + 3*s*′ + 3*d* basis)		−0·44	−0·44	0·0	−2·49	2·05
1,2,5-Oxadiazole	3·38 [g]	−2·96	−2·96	0·0	−4·46	1·50
1,3,4-Oxadiazole	3·04 [i]	2·75	+2·75	0·0	0·26	2·49
1,2,4-Oxadiazole	1·2 [c]	1·18	−0·16	+1·17	−2·45 (−70·6°) [a]	2·21 (+80·0°) [a]
1,2,3-Oxadiazole		3·70	−0·22	+3·69	−3·96 (−35·8°) [a]	−2·16 (+77·2°) [a]
1,3,4-Thiadiazole (*sp* basis)	3·28 [i]	3·38	3·38	0·0		
(*sp* + *d* basis)	3·28 [j]	4·23	4·23	0·0		
1,2,5-Thiadiazole (*sp* basis)	1·57 [k]	−2·53	−2·55	0·0		
(*sp* + *d* basis)	1·57 [k]	−1·75	−1·75	0·0		
Phosphole (planar)		1·40	1·40	0·0	−0·70	2·23
Phosphole (PH out-of-plane)		1·14	−0·54	1·00(μ_z)		
1,6,6a-Trithiapentalene (*sp* basis)	3·01 [l]	−3·87	−3·87	0·0		
(*sp* + *d* basis)	3·01 [l]	−2·17				
1,6a,6-Dithiaoxapentalene (*sp* basis)	3·78 [m]	−4·32	−3·78	−2·09		
(*sp* + *d* basis)	3·78 [m]	−3·70				
6a,1,6-Thiadioxapentalene (*sp* basis)		−3·22	−3·22	0·0		
(*sp* + *d* basis)		−2·75				
1,6a,6-Dithia-azapentalene (*sp* basis)		−4·23	−1·59	−3·92		
(*sp* + *d* basis)		−3·02				

[a] Angles with respect to positive direction of $\mu_\parallel$ and measured anticlockwise; the sign of the dipole moment is taken with the negative end in the positive cartesian direction as positive. [b] Refs. 1—3. [c] Ref. 23. [d] Ref. 24. [e] Ref. 25. [f] Ref. 1. [g] E. Saegebarth and A. P. Cox, *J. Chem. Phys.*, 1965, **43**, 166. [h] Approximate value estimated from the dipole moments of 1*H*-tetrazole and 1- and 2-ethyltetrazoles (ref. **1**). [i] B. Bak, J. Tormod Nielsen, O. Faurskov Nielsen, L. Nygaard, J. Rastrup-Anderson, and P. A. Steiner, *J. Mol. Spectroscopy*, 1966, **19**, 458. [j] B. Bak, L. Nygaard, E. J. Pedersen, and J. Rastrup-Anderson, *J. Mol. Spectroscopy*, 1966, **19**, 283. [k] Sr. V. Dobyns and L. Pierce, *J. Amer. Chem. Soc.*, 1963, **85**, 3553. [l] M. Sanesi and G. Traverso, *Chem. Ber.*, 1960, **93**, 1566. [m] M. Sanesi, G. Travers, and M. Lazarone, *Ann. Chim.* (*Italy*), 1963, **53**, 548.

TABLE 2

Dipole moments (μ/D) and vector components in six-membered rings

Name	Experimental value	LCGO				
		Total μ	$\mu_\parallel$	$\mu_\perp$	μ_σ	μ_π
Pyridine	2·15 [b]	−1·82	−1·82	0·0	−1·65	−0·17
Pyridazine	4·22 [c]	−3·65	−3·65	0·0	−3·16	−0·49
Pyrimidine	2·44 [d]	−2·15	−2·15	0·0	−1·83	−0·32
1,2,4-Triazine		−2·16	−1·21	−1·79	−1·93 (−124·8°) [a]	−0·24 (−118·0°) [a]
1,2,3,4-Tetrazine		−4·01	−4·01	0·0	−3·50	−0·51
1,2,3,5-Tetrazine		−2·48	−2·48	0·0	−2·16	−0·32
1,2,3-Triazine		−4·41	−4·41	0·0	−3·87	−0·54
Phosphorin		−1·87	−1·87	0·0		

[a] Angles with respect to positive $\mu_\parallel$ and measured anticlockwise. [b] B. B. DeMore, W. S. Wilcox, and J. H. Goldstein, *J. Chem. Phys.*, 1954, **22**, 876. [c] W. Werner, H. Dreizler, and H. D. Rudolph, *Z. Naturforsch.*, 1967, **22a**, 531; K. K. Innes, *J. Mol. Spectroscopy*, 1967, **24**, 247. [d] Ref. 1.

the accumulated data[1] on solution measurements of dipole moments in azoles shows too large a variation between different reported values for each compound to lead to any interpretation based upon increments from single substituents such as a methyl group.

Before discussing the separate σ- and π-dipole moment components, it is appropriate to describe the results of the second moment calculations, in order to gain further information on the adequacy of the basis set used in the calculations. Also we describe the population analyses as the following stage since this has a considerable bearing on the question of the σ- and π-terms in dipole moments.

TABLE 3

Comparison of calculated and experimental [a] second moments

	$\langle x^2\rangle$ [b]		$\langle y^2\rangle$ [b]		$\langle z^2\rangle$ [b]	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Cyclopentadiene	43·4	41·8 ± 2·2	42·5	42·3 ± 2·2	9·89	8·4 ± 2·2
Pyrrole	40·5	38·6 ± 0·6	40·3	39·1 ± 0·6	7·95	7·4 ± 0·6
Furan	39·3	37·8 ± 0·7	38·0	36·2 ± 0·7	7·5	6·8 ± 0·7
Thiphen						
(a) Minimal basis	45·3	44·6 ± 1·2	59·5	58·6 ± 1·2	8·4	8·5 ± 1·2
(b) + $(3s' + 3d)$	45·2	44·6 ± 1·2	59·1	58·6 ± 1·2	8·45	8·5 ± 1·2
(c) Ref. 26	44·8	44·6 ± 1·2	58·8	58·6 ± 1·2	8·54	8·5 ± 1·2
Pyridine	59·7	56·2 ± 0·8	57·5	57·1 ± 0·8	9·05	7·9 ± 0·8
Pyrimidine	55·59		54·93		8·48	
Pyridazine	55·81		55·22		8·52	
1,2,5-Oxadiazole	35·01		33·43		6·48	
1,3,4-Oxadiazole	35·33		32·56		6·40	

[a] Ref. 20. [b] $y = C_2$ symmetry axis; z = out-of-plane direction.

Second Moments.—Experimental values for second moments in the present series of azines and azoles are only available for pyrrole, furan, thiophen, and pyridine; in Table 3 we report a comparison of the two sets of data with several basis set calculations for thiophen, and including cyclopentadiene as the 'parent' compound of the series. The observed and calculated values of $\langle x^2\rangle$, $\langle y^2\rangle$, or $\langle z^2\rangle$ are related by $\langle s^2\rangle_{\text{obs}} = 1{\cdot}01\ \langle s^2\rangle_{\text{calc.}} - 1{\cdot}7$ a.u. where $s = x, y,$ or z, a very satisfactory result. The agreement with the experimental values for the quadrupole moments are however very poor. The results of a larger basis set calculation[26] for thiophen show that this property is well interpreted by the theory, but is very costly to achieve at the present time. In contrast to the observations of Coulson and Glaeser[27] we consider that accurate prediction of the quadrupole moment calls for much higher precision in the calculations than do the other second moments or the dipole moment. Thus although we record the dipole moments of some azines and azoles which have not yet been obtained we doubt whether our wavefunctions for the molecules would successfully predict the quadrupole moments, although the other second moments should also be close to experiment.

Population Analysis.—In this section we analyse the systematic trends apparent in the gross and net atomic populations, investigate their origin in terms of the orbital types, and express the contributions of net atomic population in terms of bond population dipoles. The total populations in terms of neighbouring atoms are shown in Table 4; it is clear that the introduction of a nitrogen atom adjacent to a particular ring atom C, N, or O leads to a drop in the total population by *ca.* 0·10e, with surprisingly little variation.

The core orbitals $1s_x$ (where x = C, N, O, S, or P) as well as $2s_y$ and $2p_y$ (y = S or P) are almost entirely localised on the atoms x and y (populations *ca.* 1·99 for x and *ca.* 1·90 for y). The $2s_z$ and $3s_z$ levels where z = P, S, O, N, or C are also fairly heavily localised (Tables 5 and 6) although the extent varies smoothly in total population with the free atom orbital energy[28] as follows: O, 1·25e (1·24 a.u. energy); N, 0·95e (0·95 a.u.); S, 0·70e (0·88 a.u.); C, 0·40e (0·71 a.u.); and P, 0·37e (0·70 a.u.). These findings are consistent with observations of a discrete inner valency shell and core levels in

TABLE 4

Total populations as a function of neighbouring atoms

–O–	C–O–C 8·329 ± 0·006	C–O–N 8·243 ± 0·002	N–O–N 8·146
–NH–	C–N–C H 7·451 ± 0·030	C–N–N H 7·344 ± 0·050	N–N–N H 7·217 ± 0·070
N$_A$ (Azines)	C–N$_A$–C 7·240 ± 0·020	C–N$_A$–N 7·130 ± 0·02	N–N$_A$–N 7·015 ± 0·020
N$_\alpha$ (Azoles)	C–N$_\alpha$–C	C–N$_\alpha$–NH 7·145 ± 0·035	N$_\beta$–N$_\alpha$–NH 6·996 ± 0·030
N$_\beta$ (Azoles)	C–N$_\beta$–C 7·272 ± 0·001	N–N$_\beta$–C 7·178	N–N$_\beta$–N 7·061
CH (Azines)	C–C$_A$–C 7·240	C–CA–N 7·130 ± 0·02	N–C$_A$–N 7·015
C$_\alpha$H (Azoles)	C–C$_\alpha$–C	C–C$_\alpha$–N 6·149 ± 0·030	N–C$_\alpha$–N 6·011 ± 0·030
C$_\beta$H (Azoles)	C–C$_\beta$–C 6·244 ± 0·030	C–C$_\beta$–N 6·180 ± 0·100	N–C$_\beta$–N 6·095 ± 0·020

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X-ray and $\mathrm{He^{II}}$ photoelectron spectroscopy[29-32] of heterocyclic molecules. Thus the principal bonding arises from variations in population of the $2p$ or $3p$ orbitals on the first and second row atoms and $1s_H$.

The constant increments in total population arising from the data of Tables 5 and 6 have been converted into an average set of bond population dipoles. Thus using the classical representations, in which the grouping $>\!\dot{\mathrm{N}}\mathrm{H}$ and $>\!\ddot{\mathrm{O}}$ provide 2π electrons while $\geqslant\mathrm{N}\colon$ provides 1, enables us to compare the bond polarisation *relative* to this unpolarised classical structure with a complete separation of σ- and π-systems. For example, in the σ-system of pyrrole the hydrogen H_N has a net population of $+0{\cdot}3298$e, so that this is balanced by $-0{\cdot}3298$e at the nitrogen atom. The remaining σ net population of the latter ($-0{\cdot}4260$e) arises from polarisation of each of the C–N bonds in the sense $\overset{\delta+}{\mathrm{CH}}\text{–}\overset{\delta-}{\mathrm{N}}$ where $\delta\pm = \pm 0{\cdot}2130$e.

TABLE 5

Population analysis for six-membered ring heterocycles

	C_5H_5N			
	N	C-2,-6	C-3,-5	C-4
$1s + 2s$	3·5116	3·0526	3·0632	3·0563
$2p$	2·7303	2·0325	2·1636	2·1695
$2p$	0·9933	1·0094	0·9984	0·9911
H		0·7813	0·7821	0·7818

	$1,2\text{-}C_4H_4N_2$		
	N-1,-2	C-3,-6	C-4,-5
$1s + 2s$	3·5392	3·0444	3·0642
$2p$	2·5787	2·0541	2·1782
$2p$	1·0109	1·0074	0·9817
H		0·7722	0·7692

	$1,3\text{-}C_4H_4N_2$			
	N-1,-3	C-2	C-4,-6	C-5
$1s + 2s$	3·5339	3·0162	3·0526	3·0689
$2p$	2·6947	1·9766	2·0704	2·1676
$2p$	1·0156	1·0060	0·9760	1·0107
H		0·7622	0·7676	0·7701

	$1,2,3\text{-}C_3N_3N_3$			
	N-1,-3	N-2	C-4,-6	C-5
$1s + 2s$	3·5444	3·5584	3·0484	3·0565
$2p$	2·5754	2·4379	2·0700	2·1978
$2p$	1·0093	1·0221	0·9862	0·9869
H			0·7550	0·7628

	$1,2,4\text{-}C_3H_3N_3$					
	N-1	N-2	N-4	C-3	C-5	C-6
$1s + 2s$	3·5516	3·5437	3·5085	3·0354	3·0444	3·0449
$2p$	2·5691	2·5874	2·7443	1·9443	2·0729	2·0746
$2p$	0·9953	1·0040	0·9848	1·0181	0·9930	1·0049
H				0·7548	0·7614	0·7626

	$1,3,5\text{-}C_3H_3N_3$	
	N-1,-3,-5	C-2,-4,-6
$1s + 2s$	3·5271	3·0080
$2p$	2·7080	2·0220
$2p$	1·0158	0·9841
H		0·7344

	$1,2,4,5\text{-}C_2H_2N_4$		
	N-1,-2,-4,-5	C-3,-6	N-1,-3
$1s + 2s$	3·5465	3·0187	3·5561
$2p$	2·5814	2·0052	2·5610
$2p$	0·9875	1·0251	1·0222
H		0·7205	

	$1,2,3,5\text{-}C_2H_2N_4$		
	N-2	N-4	C-4,-6
$1s + 2s$	3·5650	3·5346	3·0457
$2p$	2·4492	2·7123	1·9533
$2p$	0·9923	0·9942	0·9844
H			0·7431

	$1,2,3,4\text{-}C_2H_2N_4$		
	N-1,-4	N-2,-3	C-5,-6
$1s + 2s$	3·5526	3·5661	3·0439
$2p$	2·5735	2·4307	2·0880
$2p$	0·9903	1·0218	0·9880
H			0·7450

	CHN_5			
	N-1,-5	N-2,-4	N-3	C-6
$1s + 2s$	3·4933	3·5352	3·5333	3·0386
$2p$	2·6622	2·0524	2·4717	1·9565
$2p$	0·9774	1·0216	1·0110	0·9909
H				0·7140

	C_5H_5P			
	P	C-2,-6	C-3,-5	C-4
$1s + 2s + 3s$	5·365	3·087	3·054	3·045
$(2p + 3p)$	6·073	2·123	2·109	2·109
$(2p + 2p)$	3·002	0·991	0·974	1·009
$3d$	0·418			
$3d$	0·059			
H		0·853	0·851	0·850

The analysis thus proceeds by summation of components at the ring atoms and the solution of a series of homogeneous simultaneous linear equations for each ring atom. This analysis proceeds by inspection for the molecules with C_{2v} symmetry but algebraically for those with C_s symmetry. For the n-membered ring there are actually only $n - 1$ independent equations for the ring centres since molecular electrical neutrality makes any one centre dependent upon the negative sum of the others. The final equation requires that the vector sum round the ring atoms in a clockwise or anticlockwise direction be zero. There is no component bond dipole for the lone pair at nitrogen or oxygen since this procedure is relative to the neutral atom. Thus the vector summation of these population dipoles cannot be directly equated with the dipole moment except as a point charge approximation.

The resulting bond population moments are surprisingly reproducible from molecule to molecule (Table 7),

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[29] P. J. Derrick, L. Åsbrink, O. Edqvist, B.-Ö. Jonsson, and E. Lindholm, *Internat. J. Mass Spectrometry Ion Phys.*, 1971, **6**, 161, 177, 191, 203.

[30] J. W. Rabalais, L. O. Werme, T. Bergmark, L. Karlsson, and K. Siegbahn, *Internat. J. Mass Spectrometry Ion Phys.*, 1972, **9**, 185.

[31] U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, *Physica Scripta*, 1971, **3**, 237.

[32] D. T. Clark, and D. M. J. Lilley, *Chem. Phys. Letters*, 1971, **9**, 234.

TABLE 6

Total populations of five-membered ring heterocycles

Furan

	O	C-2,-5	C-3,-4
$1s + 2s$	3·7302	3·0456	3·0620
$2p_\sigma$	2·8936	1·8946	2·1255
$2p_\pi$	1·6996	1·0737	1·0765
H		0·7709	0·7895

Pyrrole

	N	C-2,-5	C-3,-4
$1s + 2s$	3·3980	3·0249	3·0500
$2p_\sigma$	2·4540	1·9172	2·0638
$2p_\pi$	1·6280	1·0960	1·0900
H	0·6702	0·8364	0·8465

Pyrazole

	N-1	N-2	C-3	C-4	C-5
$1s + 2s$	3·3647	3·5876	3·0089	3·0334	3·0054
$2p_\sigma$	2·4075	2·3913	2·1391	2·1334	2·0850
$2p_\pi$	1·5313	1·1463	1·1161	1·1143	1·0920
H	0·6150		0·7227	0·7702	0·7357

Imidazole

	N-1	N-3	C-4	C-4	C-5
$1s + 2s$	3·3798	3·5516	3·0093	3·0238	3·0283
$2p_\sigma$	2·4569	2·6209	1·8816	2·0574	2·0040
$2p_\pi$	1·5848	1·1005	1·0881	1·1326	1·0940
H	0·6441		0·7942	0·7640	0·7842

1*H*-1,2,4-Triazole

	N-1	N-2	N-4	C-3	C-4
$1s + 2s$	3·3661	3·5869	3·5521	3·0034	2·9916
$2p_\sigma$	2·3893	2·4420	2·6235	1·9861	1·9748
$2p_\pi$	1·5820	1·1032	1·0965	1·1300	1·0882
H	0·6130			0·7389	0·7368

2*H*-1,2,3-Triazole

	N-1,-3	N-2	C-4,-5
$1s + 2s$	3·5782	3·4188	3·0336
$2p_\sigma$	2·5397	2·0643	1·9278
$2p_\pi$	1·0675	1·6633	1·1009
H		0·5234	0·5977

1*H*-1,2,3-Triazole

	N-1	N-2	N-3	C-4	C-5
$1s + 2s$	3·3653	3·5856	3·5341	3·0006	3·0134
$2p_\sigma$	2·3841	2·2095	2·5438	2·0595	2·0671
$2p_\pi$	1·5861	1·1313	1·0924	1·1320	1·0582
H	0·6155			0·7661	0·7555

2*H*-1,2,3,4-Tetrazole

	N-1	N-2	N-3	N-4	C-5
$1s + 2s$	3·5861	3·3456	3·5722	3·5793	3·0167
$2p_\sigma$	2·4428	2·3573	2·3697	2·4767	1·9521
$2p_\pi$	1·1099	1·5865	1·0798	1·1207	1·1031
H		0·5561			0·7454

1*H*-1,2,3,4-Tetrazole

	N-1	N-2	N-3	N-4	C-5
$1s + 2s$	3·3694	3·5810	3·5713	3·5866	3·0123
$2p_\sigma$	2·4141	2·3216	2·3983	2·4612	1·9608
$2p_\pi$	1·6263	1·1174	1·0913	1·1373	1·0277
H	0·5830				0·7403

Thiophen

sp Basis	S	C-2,-5	C-3,-4
$1s + 2s + 3s$	5·755	3·106	3·053
$(2p + 3p)_\sigma$	6·365	2·039	2·075
$(2p + 3p)_\pi$	3·737	1·094	1·037
$3d_\sigma$			
$3d_\pi$			
H		0·827	0·840

Thiophen

spd Basis	S	C-2,-5	C-3,-4
	5·396	3·079	3·054
	6·355	2·007	2·074
	3·737	0·962	1·055
	0·452		
	0·039		
		0·837	0·846

Phosphole (planar)

	P	C-2,-5	C-3,-4
$1s + 2s + 3s$	5·069	3·070	3·060
$(2p + 3p)_\sigma$	5·803	2·055	2·058
$(2p + 3p)_\pi$	3·691	1·070	1·010
$3d_\sigma$	0·407		
$3d_\pi$	0·050		
H	0·826	0·853	0·851

Phosphole (PH out-of-plane)

	P	C-2,-5	C-3,-4
	5·254	3·080	3·073
	} 9·213	3·134	3·075
	} 0·523		
	0·878	0·853	0·850

1,3,4-Oxadiazole

	O-1	N-3,-4	C-2,-5
$1s + 2s$	3·7317	3·5738	3·0428
$2p_\sigma$	2·9172	2·5151	1·8064
$2p_\pi$	1·6867	1·0895	1·0672
H			0·7375

1,2,5-Oxadiazole (unscaled minimal)

	O-1	N-2,-5	C-3,-4
$1s + 2s$	3·7827	3·6101	3·0473
$2p_\sigma$	2·6082	2·3616	2·0409
$2p_\pi$	1·7549	1·0561	1·0665
H			0·7446

1,2,4-Oxadiazole

	O-1	N-2	N-4	C-3	C-5
$1s + 2s$	3·7551	3·6065	3·5299	3·0241	3·0506
$2p_\sigma$	2·7911	2·3371	2·6704	1·9441	1·8167
$2p_\pi$	1·6951	1·1060	1·0952	1·0736	1·0301
H				0·7460	0·7286

1,2,3-Oxadiazole

	O-1	N-2	N-3	C-4	C-5
$1s + 2s$	3·7585	3·6047	3·5120	3·0715	3·0638
$2p_\sigma$	2·7705	2·1916	2·5777	1·9992	1·9511
$2p_\pi$	1·7160	1·1243	1·0507	1·1150	0·9940
H				0·7503	0·7491

and the *maximum* deviation from the average value is usually *ca.* 10% for the major terms. The only example where a systematic trend rather than random fluctuation was noted was in the CH bond and NH bond populations in the azoles where the former is too variable to quote a usable average, and the latter moment increases slightly as the number of nitrogen atoms in the ring increases. Clearly the XH (X = C or N) bonds are effectively electron sinks with respect to the remainder of the molecule. The σ-set of population moments ($X_{\delta+}Y_{\delta-}$) show the expected order from electronegativity considerations of the atoms X and Y, except that the $N_\alpha N(H)$ bond is also strongly polarised in contrast to $N_\alpha N_\beta$. There is in fact a general polarisation towards the 1-position of the ring, in the σ-system, and this leads to clear differences in the polarisation of $C_\alpha N_\beta$ and $C_\beta N_\alpha$, and the $C_\alpha N(H)$ bond is more heavily polarised than either. The π-system is polarised in the reverse direction with a flow from the 1-position to the β-positions; these observations are consistent with those using the full dipole operator based upon the classical structures for partition of the nuclear component.

Dipole Moments. The σ- *and* π-*Contributions*.—The results for the azines both by the bond populations and the μ_σ and μ_π contributions show that the nitrogen atoms are electron acceptors by both σ- and π-mechanisms, and that the diazine results can be obtained by vector addition of the pyridine data. Furan shows the expected strong σ-attraction to the oxygen atom which is incompletely offset by a π-back donation. For pyrrole, the π-moment is slightly larger, probably a result of the lower electronegativity of the nitrogen atom when compared with oxygen. As is clearly shown in the population analysis, the σ-moment is the resultant of opposing moments, particularly in the NH and CN bonds and hence is numerically small. Although we have not carried out an SCF calculation on *N*-methylpyrrole, there is no reason to doubt that the dipole moment (2·12 D,[33] to be compared with 1·80 D for pyrrole) would be successfully determined by the LCGO method. This conclusion follows from our previous work on the hypothetical molecule 3*H*-sydnone and on 3-methylsydnone[34] where the increase in dipole moment (along the *N*–methyl axis) is 0·30 D for the replacement of hydrogen by methyl. This effect arises, not solely from a high CN moment, but from the additive effects of three CH and the CN bond moments.

We have considered two geometric arrangements for

TABLE 7

Bond population moments

σ System							
azines ($X^{\delta+}$ — $Y^{\delta-}$)							
X–Y	H–C	C–N	N–N	C–C			
	0·241	0·121	0·004	0·007			
No of points	29	30	7	11			
Maximum deviation	0·023	0·015	0·003	0·003			
Azoles $X^{\delta+}$ — $Y^{\delta-}$							
X–Y	C_α–O	N_α–O	C_α–N(H)	N_α–N(H)	C_α–N_β	C_β–N_α	N_β–N_α
	0·317	0·209	0·244	0·133	0·070	0·159	0·034
No. of points	7	4	8	6	6	6	4
Maximum deviation	0·010	0·070	0·015	0·016	0·018	0·026	0·019
X–Y	H–N	C_β–N_β	N_β–N_β				
	0·386	0·115	0·007				
No. of points	7	6	2				
Maximum deviation	0·050	0·004	0·007				
π System azines							
X–Y	C–N	C–C	N–N				
	0·004	0·008	0·012				
No. of points	30	11	7				
Maximum deviation	0·03	0·010	0·010				
Azoles ($X^{\delta+}$ — $Y^{\delta-}$)							
X–Y	O–C_α	(H)N–C_α	(H)N–N_α	O–N_α	C_α–C_β	N_α–C_β	
	0·142	0·195	0·219	0·148	0·103	0·087	
No. of points	6	8	6	3	8	6	
Maximum deviation	0·014	0·023	0·030	0·030	0·026	0·020	
X–Y	C_α–N_β	N_α–N_β	C_β–C_β	N_β–C_β	N_β–N_β		
	0·107	0·089	0·0	0·006	0·0		
No. of points	6	4	1	6	1		
Maximum deviation	0·029	0·030	0·0	0·008			

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[33] W. Arnold, H. D. Dreizler, and H. D. Rudolph, *Z. Naturforsch.*, 1968, **23a**, 301.

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

phosphole; one is based upon the 1-benzyl derivative[35] which had pyramidal phosphorus with both P and H out of plane with respect to the hydrocarbon skeleton. Phosphole itself is as yet unknown, but it is of interest to compare the above geometry with a planar form; thus using the same lengths and hydrocarbon angles we performed a calculation on planar phosphole. The total energy difference (32 kcal mol^{-1}) showed that the non-planar form was preferred. Thus it appears that planar phosphole is likely to be low in aromaticity. Like pyrrole, furan, and thiophen, planar phosphole has a high π-dipole moment with phosphorus as donor, which is partially offset by the σ-moment. Although the small dipole moment of thiophen is as expected in view of the near equality of electronegativity of sulphur and carbon, it is surprising to find that the small resultant moment arises from the near cancellation of large π- and σ-moments. It is worth noting that the π-dipole moment is only slightly affected by the size of basis set and whether *d* orbitals are included or not (also confirmed in the data of ref. 26) since the contribution of $3d_\sigma$ orbitals to the bonding is uniformly small; thus the marked change in dipole moment with basis set is solely attributable to the σ-bond polarisation; the calculated level of this polarisation decreases as the basis set is increased, and the experimental dipole moment is nearly obtained with large basis sets. Thus we obtain a moment only 0·1 D in error with our biggest basis set, and our result is very similar on a population basis also to that of Gelius *et al.*[26] if most of our $3d_\sigma$ contribution is transferred to the 3*s* level; that is, our $3d_\sigma$ orbitals are compensating for the small gaussian set used for the σ-system and the 3*s* level in particular. Within the framework of the σ- and π-separation of dipole moments we consider that the high σ- and π-moments for thiophen are realistic; the π-moments are all very similar in the series pyrrole, furan, thiophen, and phosphole, and the electronegativity of sulphur being close to that of carbon requires that the σ-skeleton be considerably polarised in the reverse direction to the π-moment.

The high π-dipole moments are partly a feature of the method of carrying out the σ–π separation, but mainly are an indication of the aromatic character of the ring with a valency shell of six π-electrons heavily delocalised being advantageous. Some indication of the aromaticity of these systems is possible from the extent of delocalisation as indicated from the average position of the valency shell π-electrons. Since the principal differing geometric factor is the X–C$_\alpha$ bond where X = NH, O, PH, or S, it is convenient to express these positions relative to the C$_\beta$C$_\beta$ bond, as shown in Table 8. The overall average position of the π-electrons is near C$_\alpha$ in each of the four molecules; more significant is the degree to which these six electrons separate into a group of four and a pair of electrons. In each molecule the orbital with highest heteroatom character (from the eigenvectors) also has the closest average position to that atom, and is separated from the average of the quartet by 0·34 (thiophen), 0·68 (pyrrole), 0·84 (furan), and 0·82 Å (planar phosphole). Thus the π-sextet behaves as a group best in thiophen, with pyrrole, and then furan and phosphole having increasing amounts of diene plus lone pair character. It seems possible that this type of observation could be used as a criterion for aromaticity, since the above order coincides with that from reactivity considerations such as Diels–Alder reactions.[36]

TABLE 8

Average position of the π-electrons from the C$_\beta$C$_\beta$ bond [a]

	Pyrrole (Å)	Furan (Å)	Thiophen (Å)	Planar phosphole (Å)
π_1 [b]	1·516	1·630	1·169	0·867
π_2 [b]	0·679	0·660	1·395	1·704
π_3 [b]	0·966	0·917	0·941	0·902
Average position	1·053	1·069	1·169	1·157
C$_\alpha$ co-ordinate	1·319	1·302	1·266	1·226
X co-odinate	2·107	2·127	2·455	2·480

[a] Co-ordinates of C$_\beta$ = 0 along the C_2 symmetry axis. [b] π_1, π_2, π_3 in increasing order of binding energy.

The remaining azoles have a more complex breakdown of the σ- and π-moments since the directions of these two are not coaxial. Thus for all compounds the π-moment runs along an axis through the 1-position (O or NH) and towards the midpoint of the 3,4-bond (*i.e.* not far from $\mu_{\|}$) irrespective of the siting of the heteroatoms. In contrast the σ-moment is distorted from the axis $-\mu_{\|}$ towards $+\mu_{\perp}$ quite sharply by an α-nitrogen atom. The relative directions and magnitudes of the σ-moments are readily understood in terms of the bond population moments of Table 7.* For the azapyrroles the NH bond polarity probably remains (from the population analyses) while replacement of an α-carbon atom by nitrogen leads to a marked reduction of the σ-bond moment towards nitrogen (the population analysis suggests +0·133e instead of +0·244e) and hence leads to the σ-moment being rotated towards an α-nitrogen atom through the residual effect of $\mu_{\mathrm{CN(H)}} - \mu_{\mathrm{NN(H)}}$ as observed in Table 1. Thus the σ-moment of 1,2,4-triazole is interpreted by vector addition of the C$_\alpha$–N$_\beta$ and C$_\beta$–N$_\beta$ population moments and addition of the resultant to the pyrazole σ-moments.

The σ- and π-moments are as expected for the interplay of the competing electronegativities and nuclear charges for the 1,2,5- and 1,3,4-oxadiazoles; the 1,2,5-isomers having high σ-moments and small π-moments, the latter arising from the competing requirements of highly electronegative nitrogen atoms at the 2,5-positions and the requirement for π-electron drift to the 3,4-positions as in furan *etc.*

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* Conversion of the bond population dipoles $\mu = ker$ where k = fraction of electronic charge separated by distance r (Å) to Debye units (10^{-8} e.s.u. cm) has $k = 4{\cdot}80298 \times 10^{-10}$ e.s.u.

[35] P. Coggan, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, 1970, **92**, 5779; see also W. P. Ozbirn, R. A. Jacobson, and J. L. Clardy, *Chem. Comm.*, 1971, 1062.

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

As mentioned above we are only able to report the total dipole moments of the oxa-, thia-, and aza-pentalene derivatives (*e.g.* thiathiophthen). The data in Table 1 show that these moments are high and sensitive to the size of basis set with the ($sp + d$) basis overcompensating for the shortness of the sp basis in some cases; we can be certain that the sign of the moments, with negative end of the dipole towards the heteroatoms in all cases, are correctly evaluated.

Conclusions.—The minimal basis set LCGO calculations give good agreement between the calculated and experimental dipole moment absolute values, and also agree well with the second moments except the quadrupole moment. The signs of the dipole moments for the azines and azoles of C_{2v} symmetry reported in Tables 1 and 2 are thus firmly established by the LCGO calculations, while the predictions of in-plane vector components in the molecules with C_s symmetry await confirmation by microwave spectroscopy. The use of classical structures as a reference system leads to the prediction of large π-dipole moments, which seem to be a characteristic of the molecules. The separation of the π-electron sextet into a quartet and doublet as evidenced by their average positions shows promise as an extra measure of classical as opposed to aromatic character. The net atomic populations are sufficiently additive from molecule to molecule to give effectively constant bond contributions.

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