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THE ELECTRONIC STRUCTURE OF SOME SULPHUR-CONTAINING HETEROCYCLES

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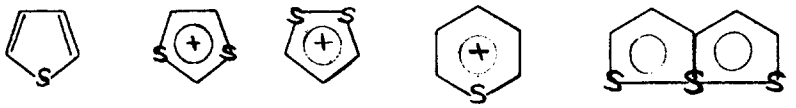
The question of whether d-orbitals play an important role in the ground state bonding of the compounds thiophene (1), 1, 3-dithiolium cation (2), 1, 2-dithiolium cation (3), thiapyrylium cation (4) and thiathiophthene (5) has aroused much controversy.[1-4] We now report a series of non-empirical calculations for these molecules.



(1) (2) (3) (4) (5)

The procedure uses a linear combination of gaussian orbitals (LCGO) with 10s- and 6p-type for sulphur, 7s- and 3p-type for carbon, and 3s-type for hydrogen, which were then contracted to the normal 1s, 2s, 3s, 2p, 3p orbitals. These were then augmented with a single gaussian for each of the five 3d-orbitals where appropriate. (For computational simplicity it is conventional to use six 3d functions (x^2, y^2, z^2, xy, xz, yz) rather than the usual five. The former were then converted to the latter and an additional s-orbital (3s' orbital) by linear combinations[5]). Comparison with earlier work on furan, pyrrole and 1, 2, 5-oxadiazole[6] suggests that the results are likely to be less than 0.2% away from the Hartree-Fock limit, and that the conclusions are unlikely to be significantly changed by closer approaches. The final energies and atomic populations with and without added d-orbitals are given in Tables 1 and 2.

TABLE 1

	Total Energy (a.u.)			Binding Energy[a] (kcal/mole)		
	sp	spd	spd + 3s'	sp	spd	spd + 3s'
1	-550.0751	-550.1442	-550.1914	593	637	666
2	-908.0214	-908.1677	-908.2629	438	533	589
3	-908.1639	-908.1766	-908.2734	434	442	503
4	-588.1449	-588.2303	-588.2773	821	874	904

[a] Binding Energy = Total Energy of Molecule - Σ Total Energy of Atoms

TABLE 2

Net charges on atoms

	sp	spd	spd + 3s'		sp	spd	spd + 3s'
		(1)				(2)	
S	0.1437	0.0374	0.0275	$S_{1,3}$	0.4294	0.3130	0.3061
$C_{2,5}$	-0.2393	-0.1722	-0.1653	C_2	-0.1810	-0.1310	-0.1275
$C_{3,4}$	-0.1654	-0.1643	-0.1657	$C_{4,5}$	-0.2007	-0.0430	-0.0337
$H_{2,5}$	0.1734	0.1638	0.1632	H_2	0.2572	0.2222	0.2213
$H_{3,4}$	0.2596	0.1541	0.1541	$H_{4,5}$	0.2362	0.2350	0.2338
		(3)				(4)	
$S_{1,2}$	0.3570	0.2838	0.2789	S	0.4234	0.2928	0.2826
$C_{3,5}$	-0.1541	-0.0604	-0.0528	$C_{2,6}$	-0.1652	-0.0859	-0.0778
C_4	-0.1296	-0.1286	-0.1319	$C_{3,5}$	-0.1143	-0.1074	-0.1094
$H_{3,5}$	0.2484	0.2324	0.7685	C_4	-0.0528	-0.0577	-0.0575
H_4	0.2272	0.2170	0.2168	$H_{2,6}$	0.2531	0.2410	0.2402
				$H_{3,5}$	0.2258	0.2215	0.2213
				H_4	0.2311	0.2266	0.2265

THIOPHENE. The total energy improvement when the five 3d-orbitals are included is 44 kcal/mole, in agreement with a slightly larger calculation by Clark,[2] who however used six 3d-functions and did not report the effect of the extra s-function implicit in his calculations. We observe that a single 3s'-function is almost as important as all five 3d-functions together. Thus inclusion of the d-orbitals represents merely a gain in variational flexibility rather than significant d-orbital participation. The d-orbitals do lead to some electron redistribution and hence improve the agreement of calculated and experimental dipole moments, which are heavily dependent upon the atomic populations. The photo-electron ionisation potentials and the molecular orbital energies are in fair agreement for the first two ionisation potentials [Experimental:-[7] 8.87 ($1a_2$), 9.52 ($2b_1$); Calculated:- 9.82 ($1a_2$), 10.25 ($2b_1$)]. The calculation including d-orbitals leads to slight improvement in the agreement.

1,3-DITHIOLIUM, 1,2-DITHIOLIUM and THIAPYRYLIUM CATIONS. For these molecules the total and orbital energies show similar trends to thiophene. We thus conclude, again, that the d-orbitals are used only to a trivial extent. Almost the whole of the positive charge on these rings is shared by the sulphur and hydrogen atoms. This appears to induce a negative charge on C-2 in the 1,3-dithiolium cation. Although this cation undergoes nucleophilic substitution at C-2 these results are not incompatible since the presence of the

reagent would be expected to induce an opposite polarisation. The polarographic half-wave reduction potentials may be compared with the energy of the lowest unoccupied molecular orbital (LUMO). The LUMO energies (eV) for (2), (3), (4) are -1.47 (A_1), -0.99 (A_2), -2.66 (A_2). The experimental values[8] are -0.69V for (2) -0.12 for (3), with (4) not yet reported. Thus there is a correct prediction of sign, order and energy difference for (2) and (3). We are currently investigating the value for (4) and details will be reported later.

THIATHIOPHTHEN. The results obtained for thiathiophthen are presented in Table 3. As can be seen the approach was different, with only one d_π and one d_σ function being used. These were added to the centre sulphur atom. The effect of the d-orbitals appears to be additive and, even allowing for the different number of d-orbitals used, is much less than in the other molecules under consideration.

TABLE 3

	sp	sp + d_π	sp + d_σ	sp + d_π + d_σ
Total Energy	-1381.0944	-1381.0974	-1381.0988	-1371.1018
Binding Energy	580	582	583	585
1st I.P. ($1a_1$)	8.49	8.50	8.49	8.49
2nd I.P. ($1a_2$)	8.82	8.85	8.82	8.85

The first two ionisation potentials are also listed in Table 3. The first ionisation potential corresponds to an orbital which is predominantly the asymmetric combination of the terminal sulphur $3p_x$ atomic orbitals, ie it is the equivalent of a lone pair. Semi-empirical calculations[9, 10] also lead to a similar prediction. The d-orbitals do not alter the order of the ionisation potentials and have very little effect on the magnitude. The values obtained are in reasonable agreement with the experimental[9] values of 8.11 eV and 8.27 eV. The existence of a 2-electron 3-centre π-bond has been used to explain the bonding in thiathiophthen. However, examination of the atomic orbital co-efficients does not reveal any π-orbital with sufficiently large co-efficients to justify the existence of such a bond.

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