Ab Initio Calculations, including *d*-Orbitals, of the Electronic Structure of Thiophen

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Summary *Ab initio* molecular orbital calculations using a Gaussian basis set, of the electronic structure of thiophen indicate that 3*d*-orbitals play a minor role in the bonding in this molecule.

THE role of sulphur 3*d*-orbital participation in the ground state of thiophen has been of considerable interest to chemists for many years. Despite numerous theoretical investigations,[1a,b] at various levels of approximation there is no real consensus of opinion as to the extent of *d*-orbital participation, although the more sophisticated treatments,[1a,2] tend to agree that their inclusion has a small effect on the total energy calculated for the molecule. We now report that on the basis of an *ab initio* molecular orbital calculation on thiophen, that the 3*d*-orbitals on sulphur play a minor role in bonding in this molecule.

The calculations have been carried out using the IBMOL IV computer program,[3] and the experimental geometry.[4] The basis set of 127 Gaussian functions consisted of a twelve *s*, nine *p*, two *d* atomic set for the S atom, seven *s* three *p* atomic set for the C atoms and three *s* atomic set for the H atoms. Orbital exponents for the *s*- and *p*-functions on sulphur and carbon atoms were taken from refs. (5) and (6) respectively. The exponents for hydrogen are those from ref. (3). The *d*-orbital exponents of 0·25 and 1·00 were extrapolated from the exponents for phosphorus given by Lehn and Munsch.[7] An exponent of 0·25 has previously been suggested by Csizmadia.[8] The 127 Gaussian functions were reduced to 50 contracted Gaussians, namely a four *s*, two *p*, two *d* set for the S atom, a three *s*, one *p* set for the C atoms and a one *s* set for the H atoms. Calculations have been carried out with and without the inclusion of *d*-orbitals on sulphur. Preliminary calculations were carried out on hydrogen sulphide to check that the contracted basis set for sulphur yielded a balanced wavefunction. The total energy (at the equilibrium geometry) of −398·2682 a.u. (without *d*-orbitals) compares favourably with a recently published Slater basis set calculation,[9] (−397·905 a.u. including *d*-orbitals), with dipole moments of 1·48 D and 0·05 D respectively. The experimental quantities are −400·8 a.u.[10] and 0·98 D.[11]

The results are shown in the Table. The inclusion of *d*-orbitals on sulphur results in a small but significant lowering of the total energy of 0·1179 a.u. However in the present study twelve GTF have been used to describe *six* *d*-type orbitals (*i.e.* d_{x^2}, d_{y^2}, d_{z^2}, d_{xy}, d_{xz}, d_{yz}) of the sulphur atom rather than the usual five. It is possible to effect a linear transformation of this set[8] to a 3*s*-type ($d_{x^2} + {}_{y^2} + {}_{z^2}$) and five 3*d*-type ($d_{x^2-y^2}$, $d_{3z^2-r^2}$, d_{xy}, d_{xz}, d_{yz}) functions. A detailed analysis will be presented at a later date, however at this stage we can say that inspection of the eigen functions shows that the major part of the energy lowering of 0·1179 a.u. arises from the increased variational freedom in the *s*-basis set due to the added 3*s*-type function. This is further illustrated by calculations we have carried out on the spherically symmetric sulphide ion (S^{2-}). The total energies with and without inclusion of *d*-functions are −396·8185 a.u. and −396·7094 a.u. In this case the energy lowering of 0·1091 a.u. arises solely from the added 3*s*-type function and the atomic populations of the d_{x^2}, d_{y^2}, and d_{z^2} functions amount to 0·355 e each.

Theoretical results for the thiophen molecule

		s,p Basis set on sulphur	*s,p,d* Basis set on sulphur
Total energy		−550·4174 a.u.	−550·5353 a.u.
Atomic populations			
S	3*s*	1·716	1·140
	$3p_x$	0·872	0·913
	$3p_y$	1·347	1·317
	$3p_z$	1·680	1·684
	$3d_{x^2}$	—	0·172
	$3d_{y^2}$	—	0·184
	$3d_{z^2}$	—	0·184
	$3d_{xy}$	—	0·108
	$3d_{xz}$	—	0·052
	$3d_{yz}$	—	0·018
Total		15.616	15·773
C-1(C-4)	2*s*	1·179	1·139
	$2p_x$	1·114	1·094
	$2p_y$	0·997	0·995
	$2p_z$	1·106	1·074
Total		6·396	6·302
C-2(C-3)	2*s*	1·096	1·093
	$2p_x$	1·023	1·022
	$2p_y$	1·076	1·077
	$2p_z$	1·054	1·049
Total		6·249	6·242
H-1(H-4)		0·769	0·784
H-2(H-3)		0·778	0·787

The small degree of participation in bonding of the five *d*-type orbitals in thiophen is also illustrated by the gross atomic populations given in the Table. It is clear that the major difference in atomic population occurs for the 3*s*-functions of sulphur. The lower contribution in the case of the calculation including *d*-orbitals is offset to a considerable extent by the population of the 3*s*-type orbital formed from the 3*d*-functions. Inclusion of π-typ e*d*-orbitals (d_{xz}, d_{yz}) results in a small shift of electron density mainly from C-1(C-4) to sulphur. However the diffuseness of the *d*-orbitals, means that this is largely a matter of definition and their population should to a large extent be associated with the C atoms. There is a small effect on the population on the hydrogen atoms on inclusion of *d*-orbitals with H-1(H-4) having the lower population in both cases. The carbon atoms overall carry a substantial negative charge arising largely from the σ-system. Excluding the 3*s*-type orbital formed from the *d*-functions, the total population of the *d*-orbitals involved in the σ-bonding is larger than for that involved in π-bonding, a feature also shown by the CNDO work.[1a]

A clear distinction between the non-empirical and semi-empirical treatments arises in the assignment of the first three energy levels of thiophen. The CNDO calculation including *d*-orbitals[1a] gives the ordering as $^{\pi}B_2$ (10·28 ev), $^{\sigma}A_1$ (10·65 ev), $^{\pi}A_2$ (10·67 ev), compared to the non empirical calculation $^{\pi}A_2$ (10·83 ev), $^{\pi}B_2$ (11·04 ev), and $^{\sigma}A_1$ (14·49 ev).†

Finally, the basis set employed in these calculations almost certainly tends to overestimate the extent of *d*-orbital participation and a near-Hartree–Fock basis set would reduce even the present small contribution of the five transformed *d*-orbitals.

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† For the basis set including *d*-orbitals; corresponding figures for the calculation without *d*-orbitals: 11·17 ev, 11·30 ev, 14·12 ev.

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