Non-empirical Calculations of the Electronic Structures of 6a-Thiothiophthen and Related Molecules

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Computations of the ground-state wavefunctions for the title compound, and its 1-oxa-, 1,6-dioxa-, and 1-aza-derivatives. are described. A bond energy analysis shows that the molecules have little resonance energy. The title compound shows two lone pair orbitals at the centre sulphur atom, but the 3*d* orbitals are not heavily involved in the bonding in this series of molecules. The photoelectron spectra are analysed and compared with the π-isoelectronic molecule naphthalene.

THE product from the reaction of phosphorus pentasulphide with heptane-2,4,6-trione was shown[1] to have the spatial arrangement (1a; $R^2 = R^5 = Me$, $R^3 = R^4 = H$) by *X*-ray crystallography. Since that time the parent compound (1a) and the related isosteres (1b—d) (R^2—$R^5 = H$) have been prepared,[2-4] and in all of the four cases the detailed electronic structure has been a controversial subject.[5] A monocyclic form with the remaining heteroatom in a transoid orientation (2c) can be envisaged but to our knowledge no species (2c) has been synthesised by routes which lead also to species like (1a—e). Since the nuclear–nuclear repulsion in (2c) is considerably less than (2a or b), it is clear that the electronic energy of (2c) is also lower and this must imply an X–S and Y–S bond (albeit weak in some instances). We recently reported[6] brief results of non-empirical MO calculations aimed at elucidation of the electronic structures of (1a—c and e; R^2—$R^5 = H$) and now give a detailed description of these studies. The principal aims of the work are therefore to determine from non-empirical wavefunctions (*a*) whether the 3*d* orbitals on the sulphur atoms make a significant contribution to the bonding; (*b*) whether the classical formulation of the molecules (1a—e) with X–S and Y–S bonds is adequate or whether representations such as 2a (or 2b) are more appropriate; (*c*) whether there is any evidence of aromaticity, provided ring strain allows this to be done; (*d*) the electronic charge distribution by Mulliken population analysis; and (*e*) an assignment for the photoelectron spectrum of the parent molecule (1a).

Of the possible names for these compounds,[1,5,7-10] for simplicity in the present work we shall refer to (1a—c and e; R^2—$R^5 = H$) as the trithia-, oxadithia-, dioxathia-, and dithia-azapentalenes since this is the briefest consistent with conveying information on the geometrical arrangement of the atoms.

Computational Methods.—We used the linear combination of gaussian orbital (LCGO) approach to the Hartree–Fock method. Carbon, nitrogen, and oxygen atoms were represented by 7 *s*-type and 9 *p*-type (3 for each of *x,y,z*) gaussian functions, hydrogen by 3 *s*-type, and sulphur by 10 *s*-type, 18 *p*-type (6 for each of *x,y,z*), and 6 *d*-type (1 for each of xy, xz, yz, x^2, y^2, z^2). These functions were contracted to $1s_x$, $2s_x$, $2p_x$ (x = C, N, O, or S), $3s_s$, $3p_s$, $3d_s$, and $1s_h$ functions, the 6 *d*-type functions on each sulphur atom providing a further *s*-type function ($3s'$) as well as the conventional 5 3*d*-orbitals ($xy,xz,yz,x^2 - y^2,z^2$).[11] The gaussian exponents were optimised in terms of total energy in ethylene (C,H), vinylamine (N), vinyl alcohol (O) as described previously,[12] and thioformaldehyde (S).† The molecular binding energy is defined as the difference between the total molecular energy (evaluated with the optimised exponents above) and the sum of the atom energies (evaluated with separately optimised exponents for the atoms using a similar number of gaussian type orbitals). These atom energies, in what is conventionally called a ' best atom ' basis, have the following total energies (with the Hartree–Fock values in parentheses): H(^2S) −0·4971 (−0·5000), C(^3P) −37·6106 (−37·6886), N(^4S) −54·2754 (−54·4010), O(^3P) −74·5121 (−74·8090), S(^3P) −396·6988 (−297·5050) a.u. It can be seen that the present basis represents >99·7% of the free atom energies at the Hartree–Fock limit.

Geometric Features.—Previous discussion has centred on the question of whether the trithia-compound (1a) has a symmetrical structure owing to resonance between the two equivalent structures (2a and b; X = Y = S) or whether there is an equilibrium between two structures (2a and b). *X*-Ray crystallographic investigations have confirmed that the parent (1a),[13] but not the 2,5-diphenyl derivative of (1a) has equal S–S bonds in the solid state.[14] A recent electron diffraction study[15] of the

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† The best total energy for thioformaldehyde was −435·6818 a.u. when the *d*-orbitals on sulphur were included, and −435·5946 a.u. when excluded.

[1] S. Bezzi, M. Mammi, and G. Garbuglio, *Nature*, 1958, **182**, 247.

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[12] (*a*) M. H. Palmer, A. J. Gaskell, and M. S. Barber, *Theor. Chim. Acta*, 1972, **26**, 357; (*b*) M. H. Palmer and R. H. Findlay, *Chem. Phys. Letters*, 1972, **15**, 416.

[13] F. Leung and S. C. Nyberg, *Chem. Comm.*, 1969, 137.

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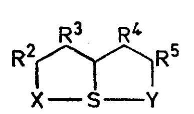
gaseous molecule (1a) confirms C_{2v} symmetry, but gave insufficient information to determine the relative lengths of the 2,3- and 3,3a-bonds. In these circumstances we feel justified in assuming the *X*-ray (symmetrical) structure for (1a).[16,*] Furthermore it seems probable that the asymmetry in the peak obtained for the S_{2p} electron levels in *X*-ray photoelectron spectra (XPS) for some derivatives[17] is a result of crystal packing forces leading to distortion. For the oxadithia- (1b), dioxathia- (1c), and dithia-aza-molecules (1e) the structures were again based upon the trithia-compound (1a), and the heteroatoms were sited to reproduce as well as possible known geometric features. In this way many of the electron repulsion integrals could be used in calculations in all four molecules (1a—c and e).

RESULTS

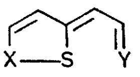
Total Energy.—This term is steadily lowered (Table 1) in (1a—c and e) as the basis set is extended from the minimal *sp* (C, N, O, and S) to extended *spd* + 3*s*′(S) where a total of eighteen extra functions are added. Several of these basis sets are unbalanced and are included only to show the nearly additive effects of functions which are —130 kJ mol^{-1} per 3*s*′ orbital (irrespective of position), —25 kJ mol^{-1} per 3*d* orbital (terminal sulphur S-1, S-6), and —30 kJ mol^{-1} per 3*d* orbital (S-6a). These figures are effectively identical† with those of similar studies[6] on thiophen, the thiapyrylium cation, and the 1,2- and 1,3-dithiolium cations, and only marginally larger than the effect of added 3*d* polarisation functions to the oxygen atom of furan (—24 kJ mol^{-1} per function).[12a] The significantly larger effect of the 3*s*′ than the 3*d* functions for the present series confirms the role of the latter as polarisation orbitals.

The 'strain plus resonance energies,' determined as outlined in the Appendix show a considerable destabilisation compared with that expected from the strain free bond contributions; most of this must be attributed to strain in the two fused five-membered rings.‡ None the less it seems unlikely that these molecules are aromatic in the normal sense; comparable figures are benzene —213, naphthalene —360, and thiophen —145 kJ mol^{-1}, which are in reasonable agreement with both mesomeric energies based upon thermochemical data (—155, —322, and —130 kJ mol^{-1})[19] and magnetic susceptibility out-of-plane nonlocal contributions (35, 79·8, and 34 erg gauss^{-2} mol^{-1}).[20]

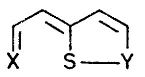
Population Analysis.—The results for the trithia-compound (1a) are typical (Table 2). Addition of 3*s*′ and 3*d* orbitals does not lead to a marked change in total populations, but to a redistribution by different mechanisms. The 3*s*′ orbital removes some population from the other sulphur *s* orbitals in the order 3*s* > 2*s* > 1*s* and this leads to an increase in valency shell population. In contrast the 3*d* orbitals redistribute the populations of $3p_{x,y,z}$ (in particular). The populations of the individual 3*d* orbitals are uniformly low, with only a significant value along the S–S–S and C–S axes ($3d_{x^2-y^2}$). The effect parallels that in a thiophen calculation[6] using the same basis set; since in the latter case a larger basis[21] reduces the 3*d* contributions, it seems probable that the present data are more likely to over- rather than under-estimate the 3*d* orbital contributions.



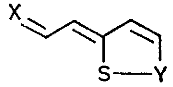
(1) a; X = Y = S
b; X = S, Y = O
c; X = Y = O
d; X = S, Y = NPh, R^2 = R^4 = Ph
e; X = S, Y = NH



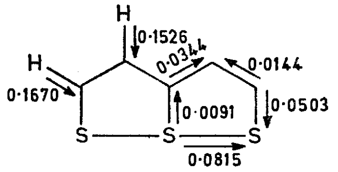
(2a)



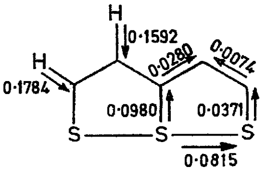
(2b)



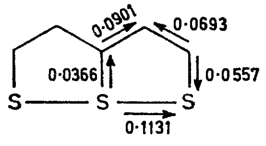
(2c)



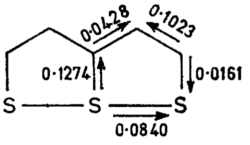
(3a) (σ + π)-bond moments
(full basis, *spd* + 3*s*′)



(3b) (σ+π)-bond moments
(minimal basis, *sp*)



(3c) π-bond moments
(full basis, *spd* + 3*s*′)



(3d) π-bond moments
(minimal basis, *sp*)

Dissection of the total σ + π and π populations into bond contributions (3a—d) shows the comparatively

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* In an unsymmetrically substituted derivative of (1a), the possibility of detecting isomers (2a and b) becomes real if their energy difference (Δ*E*) in the Boltzmann distribution $n_a/n_b = \exp(-\Delta E/RT)$ is not too large. No such pairs of isomers have yet been detected, and this tends to argue against the equilibrium hypothesis.

† Comparable figures for energy increments on added 3*s*′ and 3*d* orbitals to sulphur are: thiophen: 3*s*′, 126; 3*d*, 36; thiapyrylium cation: 3*s*′, 128; 3*d*, 45; 1,2-dithiolium cation: 3*s*′, 132; 3*d*, 42; 1,3-dithiolium cation: 3*s*′, 128; 3*d*, 38 kJ mol^{-1} respectively.

‡ We noted previously[18] the very strong similarity in the geometry of naphthalene to the hydrocarbon portion of trithiapentalene (1a); on the assumption that there is little strain in the former owing to the near natural valency angles and lengths, we conclude that the strain energy in (1a) arises from the extension of the S–S lengths (*ca.* 0·32 Å) beyond the sum of the covalent radii.

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

small differences between the minimal and most extended bases. Only with C(3a) is the net atomic population changed in sign and in view of the over-compensation in dipole moment when the $3s' + 3d$ functions are added, it seems probable that C(3a) is probably near neutral. The σ/π separation (3c and d) is based upon an average of the species (2a and b; X = Y = S) the π-atomic contributions being S(1) [= S(6)] 1·5 and S(6a) 2·0 electrons. The central sulphur atom S(6a) is a π-donor and σ-acceptor, as in thiophen.

Orbital Energies and Photoelectron Spectrum.—Addition of the $3s'$ orbital to any sulphur atom in the series (1a—c and e) increases the binding energy of the core electrons (Table 3), and slightly reduces that of the valency shell region. This last effect also occurs on addition of $3d$ orbitals but the magnitude is smaller

TABLE 1

Computed energies and dipole moments

1,6,6a-Trithiapentalene								
Basis set								
S(1), S(6)	*sp*	*sp*	*sp* + $3s'$	*sp*	*spd*	*sp*	*spd* + $3s'$	*spd* + $3s'$
S(6a)	*sp*	*sp* + $3s'$	*sp*	*spd*	*sp*	*spd* + $3s'$	*sp*	*spd* + $3s'$
Total energy (a.u.)	−1381·0944	−1381·1455	−1381·1892	−1381·1628	−1381·1883	−1381·2141	−1381·2838	−1381·4048
Binding energy (a.u.)	−0·9658	−1·0079	−1·0516	−1·0252	−1·0507	−1·0765	−1·1462	−1·2672
Strain + resonance [a] energy (kJ mol^{-1})	+220							+202 [d]
Dipole moment (D) [b,c]	−3·87	−3·87	−3·85	−3·40	−2·57	−3·40	−2·56	−2·17
6-Oxa-1,6a-Dithiapentalene								
Basis set								
S(1)	*sp*	*sp*	*sp* + $3s'$	*sp*	*spd*	*sp*	*spd* + $3s'$	*spd* + $3s'$
S(6a)	*sp*	*sp* + $3s'$	*sp*	*spd*	*sp*	*spd* + $3s'$	*sp*	*spd* + $3s'$
Total energy (a.u.)	−1059·0073	−1059·0554	−1059·0540	−1059·0647	−1059·0579	−1059·1132	−1059·1050	−1059·2111
Binding energy (a.u.)	−0·9563	−1·0044	−1·0030	−1·0137	−1·0069	−1·0622	−1·0540	−1·1601
Strain + resonance energy (kJ mol^{-1}) [a]	+226, [e] +195 [f]							+260, [e] +165 [f]
Dipole moment (D) [b,c]	4·32	4·32	4·32	3·78	4·18	3·78	4·18	3·70
1,6a-Dithia-6-azapentalene								
Basis set								
S(1)	*sp*	*sp*	*sp*	*spd* + $3s'$				
S(6a)	*sp*	*sp* + $3s'$	*spd*	*spd* + $3s'$				
Total energy (a.u.)	−1039·2279	−1039·2769	−1039·2996	−1039·4435				
Binding energy (a.u.)	−1·0165	−1·0655	−1·0882	−1·2321				
Strain + resonance energy (kJ mol^{-1}) [a]	+261, [g] +218 [h]			+263, [g] +153 [h]				
Dipole moment (D)	4·23	4·12	3·88	3·02				
1,6-Dioxa-6a-thiapentalene								
Basis set								
S(6a)	*sp*							
Total energy (a.u.)	−736·8472	−736·8938	−736·8984	−736·9440				
Binding energy (a.u.)	−0·8829	−0·9295	−0·9341	−0·9797				
Strain + resonance energy (kJ) mol^{-1}) [a]	+394 [i]							
Dipole moment (D)	3·22	3·23	2·75	2·75				

[a] For method of calculation based upon bond energies, see text. [b] The sign convention (*cf.* M. H. Palmer, R. H. Findlay, and A. J. Gaskell, *J.C.S. Perkin II*, 1974, 420) has a negative dipole moment in the sense $C^{\delta+}$—$S^{\delta-}$. [c] Experimental values are: 1,6,6a-trithiapentalene 3·01D; 6-oxa-1,6a-dithiapentalene, 3·78D. [d] Based upon 3-thioformylmethylene-1,2-dithiole. [e] Based upon 3-formylmethylene-1,2-dithiole. [f] Based upon 3-thioformylmethylene-1,2-oxathiole. [g] Based upon 3-iminomethylene-1,2-dithiole. [h] Based upon 3-thioformylmethylene-1,2-thiazole. [i] Based upon 3-formylmethylene-1,2-oxathiole.

(0·5 eV maximum total). The change in core binding energy arises directly from the decrease in screening of the nucleus through the transference of core level population to the valency shell upon addition of 3*s*′ orbitals (above).

TABLE 2

Population analyses

(*a*) 1,6,6a-Trithiapentalene *spd* + 3*s*′ basis

Centre [a]	1*s*	2*s*	3*s*	3*s*′	$2p_x$	$2p_y$	$2p_z$	$3p_x$	$3p_y$	$3p_z$	3*d*	Total	*sp* Basis Total
S(1), S(6)	1·9956	1·9243	1·5477	0·3440	1·9910	1·9842	1·9950	1·5103	1·0955	1·6543	0·0898	16·1318	16·0444
S(6a)	1·9951	1·9190	1·5824	0·3396	1·9801	1·9861	1·9957	0·9442	1·2041	1·7172	0·1643	15·8280	15·7309
C(2), C(5)	1·9892	1·0779			1·1311	1·0292	0·8750					6·1023	6·2081
C(3), C(4)	1·9888	1·0057			0·9492	1·0993	1·1594					6·2024	6·1946
C(3a)	1·9893	1·0682			1·0801	0·9441	0·8564					5·9382	6·0421

	1*s*			$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	$3d_{x^3-y^2}$	$3d_{3z^3-r^3}$
H(2), H(5) [b]	0·8300	S(1)	S(6)	0·0052	0·0030	0·0165	0·0516	0·0135
H(3), H(4) [b]	0·8474		S(6a)	0·0060	0·0085	0·0156	0·1088	0·0254

(*b*) 1,6-Dioxa-6a-thiapentalene *spd* + 3*s*′ basis

	Core (C, O, S)	Valency shell 2*s*/3*s*	3*s*′	$2p\delta/3p\delta$	$2p\pi/3p\pi$	$3d\delta$	$3d\pi$	Total	*sp* Basis Total
S(6a)	9·8883	1·5970	0·3393	1·7828	1·8735	0·0854	0·0133	15·5795	15·4983
O(1), O(6)	1·9959	1·8633		3·0822	1·5734			8·5149	8·5123
C(2), C(5)	1·9901	1·0036		2·0057	0·8061			5·8056	5·8094
C(3), C(4)	1·9987	0·9920		1·9985	1·2695			6·2487	6·2447
C(3a)	1·9894	1·0769		2·0440	0·8174			5·9277	6·0258

Hydrogen 1*s* H(2), H(5) 0·8270; H(3), H(4) 0·8502

(*c*) 6-Oxa-1,6a-dithiapentalene *spd* + 3*s*′ basis

	Core (C, O, S)	Valency shell 1*s*/2*s*/3*s*	3*s*′	2*p*/3*p*	2*p*/3*p*	3*d*	3*d*	Total	*sp* Basis Total
S(1)	9·8889	1·5457	0·3406	2·3468	1·8007	0·0790	0·0193	16·0210	15·9526
S(6a)	9·8843	1·5785	0·3383	2·0750	0·8133	0·0997	0·0176	15·8066	15·7276
O	1·9960	1·8674		3·2483	1·3943			8·5060	8·4855
C(2)	1·9891	1·0700		2·1382	0·9186			6·1159	6·2236
C(3)	1·9889	1·0118		2·0556	1·1267			6·1826	6·1758
C(3a)	1·9893	1·0674		2·0282	0·8577			5·9423	6·0448
C(4)	1·9887	0·9976		2·0344	1·2162			6·2369	6·2216
C(5)	1·9901	0·9993		1·9952	0·8419			5·8265	5·8299

Hydrogen 1*s* H(2) 0·8248; H(3) 0·8426; H(4) 0·8404; H(5) 0·8543

(*d*) 1,6a-Dithia-6-azapentalene *spd* + 3*s*′ basis

	Core (C, N, S)	Valency shell 2*s*/3*s*	3*s*′	2*p*/3*p*	2*p*/3*p*	3*d*	3*d*	Total	*sp* Basis Total
S(1)	9·8895	1·5454	0·3423	2·5965	1·7148	0·0709	0·0187	16·1689	16·1039
S(6a)	9·8797	1·5790	0·3325	2·0735	1·7481	0·1505	0·0234	15·7867	15·6786
N	1·9927	1·5250		2·4621	1·4875			7·4675	7·4502
C(2)	1·9892	1·0745		2·1525	0·8971			6·1132	6·2185
C(3)	1·9888	1·0054		2·0529	1·1592			6·2063	6·2028
C(3a)	1·9893	1·0654		2·0175	0·8688			5·9411	6·0428
C(4)	1·9888	0·9967		2·0289	1·2083			6·2227	6·2157
C(5)	1·8999	1·0455		2·0771	0·8819			5·9944	6·0005

Hydrogen 1*s* H(2) 0·8394; H(3) 0·8530; H(4) 0·8606; H(5) 0·8417; H(6) 0·7045

[a] Molecule in *xy*-plane with *y* as C_2 symmetry axis. [b] Hydrogen numbered as for attached carbon atom.

The He^{I} photoelectron spectrum of the trithia-compound (1a)[22] has been assigned previously on the basis of extended Hückel (EHM) and CNDO/2 calculations; the spectrum has yielded IPs at 8·11, 8·27, 9·58, and 10·01 eV with groups centred on 11·1, 12·8, 15·3, and 16·8 eV. Our minimal basis set calculation orbital energies (Table 3), through the use of Koopmans' theorem, reproduce the relative spacings of these IPs satisfactorily,* and lead to the correlation line based upon the first four IPs of $IP_{obs} = 0{\cdot}546\ IP_{calc} + 3{\cdot}46$ eV. To extend the assignment to higher IPs it is necessary to assign the groupings as follows: 11·1 (two IPs), 12·8 (four IPS), 15·3 (three IPs), 16·8 eV (two IPs), which are reasonable in the light of the band intensities. This leads to the final correlation line (Figure 1) $IP_{obs} = 0{\cdot}605\ IP_{calc} + 2{\cdot}775$ eV with standard deviations in slope, intercept, and overall of 0·009, 0·100, and 0·049 eV, respectively. The present correlation line slope shows the progressive decrease expected with the size of the molecule studied.[23,24] This arises from the size of basis set in which the percentage difference from the Hartree–Fock limit is nearly constant (99·5%), but the absolute error is increasing, as also is the correlation energy which also would lead to correction in the right sense. None

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* For the reasons described above the full basis set is probably somewhat unbalanced, and does not reproduce the groupings satisfactorily, although a correlation line $IP_{obs} = 0{\cdot}585\ IP_{calc} + 3{\cdot}15$ eV can be obtained.

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TABLE 3

(*a*) Canonical orbital energies (eV) and character for 1,6,6a-trithiapentalene

sp Basis	*spd* + 3*s*′ Basis	Character [a]	*sp* Basis	*spd* + 3*s*′ Basis	Character [a]
a_1	a_1		b_2	b_2	
−2493·9	−2496·7	$1s_{6a}$	−2490·0	−2493·4	$1s_{1-6}$
−2490·0	−2493·4	$1s_{1+6}$	−309·4	−309·1	$1s_{2-5}$
−310·2	−309·9	$1s_{3a}$	−308·0	−307·5	$1s_{3-4}$
−309·3	−309·1	$1s_{2+5}$	−235·5	−236·3	$2s_{1-6}$
−308·0	−307·5	$1s_{3+4}$	−181·3	−181·9	$2p_{6a}$
−239·0	−239·4	$2s_{6a}$	−177·9	−178·9	$2p_{1+6}$
−235·6	−236·3	$2s_{1+6}$	−177·9	−178·9	$2p_{1-6}$
−181·3	−181·9	$2p_{6a}$	31·67	−31·05	CC(2*s*)
−177·9	−178·9	$2p_{1+6}$	−26·32	−25·87	SS(3*s*)
−177·8	−178·9	$2p_{1-6}$	23·40	−22·94	CH(2*p*, 1*s*)
−33·66	−32·91	CC(2*s*)	19·90	−19·53	CH(2*p*, 1*s*)
−28·94	−28·30	CC(2*s*)	−17·23	−16·66	CC(2*p*)
−28·16	−27·59	SS(3*s*)	−15·79	−15·64	CS
−22·87	−22·48	CS(2*p*, 3*s*)	−12·97	−13·01	$3p_{1-6}$ + SS (3*p*)
−21·15	−20·88	CH(2*p*, 1*s*)			
−20·21	−19·68	CH(2*p*, 1*s*)			
−15·59	−15·42	CS(2*p*, 3*p*)			
−14·04	−14·32	CS (2*p*, 3*p*)	b_1	b_1	
−9·49	−8·51	$3p_{1+6}$	−181·2	−181·8	$2p_{6a}$
a_2	a_2		−177·8	−178·8	$2p_{1+6}$
−177·8	−178·8	$2p_{1-6}$	−16·63	−16·02	CC + CS
−14·03	−13·62	CS	−12·05	−11·37	$3p_{6a}$
−8·82	−8·54	$3p_{1-6} + 2p_{3-4}$	−11·23	−10·84	$3p_{1+6}$

(*b*) Canonical orbital energies (eV) for 1,6-dioxa-6a-thiapentalene (*sp*) basis)

a_1	Character [a]	b_2	Character	b_1	Character [a]
−2496·0	$1s_{6a}$	−559·8	$1s_{1-6}$	−183·1	$2p_{6a}$
−559·8	$1a_{1+6}$	−311·4	$1s_{2-5}$	−17·23	CO(2*p*) + CS(2*p*, 3*p*)
−311·4	$1s_{2+5}$	−307·3	$1s_{3-4}$	−14·05	CO(2*p*) − CS(2*p*,3*p*)
−310·7	$1s_{3a}$	−183·2	$2p_{6a}$	−12·05	SO(3*p*,2*p*)
−307·3	$1s_{3+4}$	−38·05	$2s_{1-6}$		
−183·2	$2p_{6a}$	−29·24	CC(2*s*)		
−38·14	$2s_{1+6}$	−23·94	CH_{2-5}(2*p*,1*s*)	a_2	
−32·32	(CC + CS)(2*s*,3*s*)	−20·24	CH_{3-4}(2*p*,1*s*)	−16·10	CO
−28·48	$3s_{6a}$ + CC(2*s*)	−17·62	CC(2*p*)	−9·16	$2p_{1-6}$ − CC
−24·84	$CH_{2+5} + 3s_{6a}$	−17·04	CO)2*p*,2*p*)		
−21·09	(CH_{2+5} + CC)(2*p*,1*s*)	−13·54	$2p_{1-6}$ + SO(3*p*,2*p*)		
−20·80	(CH_{3+4} + CC)(2*p*,1*s*)				
−16·64	CO(2*p*,2*p*)				
−15·78	CS(2*p*,3*p*)				
−11·78	$2p_{1+6}$				

(*c*) Canonical orbital energies (eV) for 6-oxa-1,6a-dithiapentalene (*sp* basis)

Symmetry				Symmetry
a′	*a*′	*a*′	*a*′	*a*″
−2493·8	−238·9	−37·41	−20·54	−181·1
−2492·0	−237·4	−33·37	−20·08	−179·6
−559·0	−181·2	−30·48	−17·42	−16·72
−310·7	−181·2	−16·51	−15·01	−28·27
−310·0	−179·7	−15·51	−12·96	−27·68
−309·6	−179·7	−15·02	−11·80	−23·93
−308·5		−13·46	−9·01	−23·42
−307·4		−11·08		−21·14

(*d*) Canonical orbital energies (eV) for 1,6a-dithia-6-azapentalene (*sp* basis)

Symmetry					—Symmetry
a′	*a*′	*a*′	*a*′	*a*′	*a*″
−249·36	−306·9	−33·56	−20·98	−13·01	−180·9
−2488·9	−238·6	−31·80	−20·08	−8·80	−176·8
−422·3	−234·6	−28·95	−19·49		16·07
−309·6	−180·9	−27·98	−16·98		−13·75
−309·3	−180·9	−26·43	−16·38		−11·45
−308·5	−177·0	−23·48	−15·42		−10·83
−307·2	−176·9	−22·55	−14·92		−8·02

[a] Core and other localised orbitals are indicated by orbital type and the centre. Valency shell delocalised orbitals show the principal centres involved and the orbitals in parentheses. For simplicity this has been restricted to the C_{2v} symmetry molecules; use of the correlation diagram (Figure 2) enables the principal character of other orbitals to be determined.

the less, the present correlation reproduces the orbital groupings better than either the EHM or CNDO/2 earlier calculations.*

The solid-phase XPS [17,25] separation of $2p_{6a}$ from $2p_{1,6}$ is 1·5, 1·5, and 0·9 eV in (1a), its 2,5-dimethyl derivative, and the 2,5-dimethyl derivative of (1b); a figure of 0·9 eV for (1b) is thus reasonable, and the present calculations indicate a smaller separation between these core levels in (1b) than (1a).

Conclusions on the Effect of the 3d *Orbitals*.—The above data show that although the addition of extra functions (3*s*′ and 3*d*) to the minimal basis improves (*i.e.* lowers) the total energy, the effect is very small (*ca.* 0·03%) although much more in binding energy terms. However, almost all this can be attributed to the 3*s*′ function and *not* to the 3*d* orbitals. On this basis alone we conclude that the 3*d* orbitals are not playing a major role in the bonding; their effect is to improve, but not alter the character, of the occupied molecular orbitals. This is what is usually defined as the role of polarising functions, which by virtue of the higher angular functions (*d* character) move some electron density off the internuclear axes. The results for the population analyses again show the small role of the 3*d* orbitals. There are strong indications that these conclusions are correct, since had the 3*d* functions played a major bonding role we would have expected that the addition of them would have led to better agreement with the experimentally measurable quantities such as IPs and the dipole moment. However, consistent with the polarising nature we find that the inclusion of 15 3*d* orbitals in (1a) unbalances the basis set considerably. Further evidence that this is the case arises from the dipole moments for (1a) where the dipole moment goes from too large (minimal *sp* basis) to too small (*spd* + 3*s*′ basis). Thus although the best total energies are obtained from the more flexible largest bases, it seems probable that the most balanced wave functions lie near the *sp*(or *sp* + 3*s*′) ones, the extra 3*s*′ orbital being advantageous for the larger second row atoms to avoid undue inflexibility. The addition of polarisation functions to C, H, *etc.* would probably restore the balance to the largest set, but is unlikely to lead to more than marginal new information.

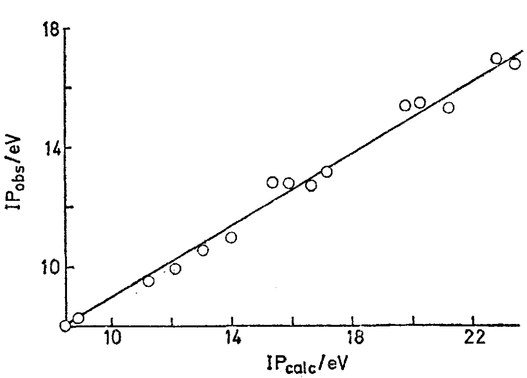

FIGURE 1 Comparisons of calculated and experimental IPs

There is some confusion over the question of whether non-empirical calculations show evidence of 3*d* orbital participation in bonding by the second row elements Si, P, S, and Cl other than in a purely polarisation sense. Here we have defined bonding participation as being one where large eigenvectors (*or* populations) are apparent for the 3*d* orbital component. Some authors have concluded that the 3*d* orbitals are important in molecules not too dissimilar to this and our earlier work, on the basis of the lowering of energy when the *six* 3*d* orbitals are included in the molecular computation.[26] It is important that these energy differences are consistently analysed; within the gaussian-type orbital (GTO) system of *six* 3*d* orbitals there is an implicit *s* function (here called 3*s*′) corresponding to $3d_{x^2+y^2+z^2} = 3d_{r^2}$. Unless this linear combination is removed by the standard method of contraction [11] of six 3*d* GTOs to 3*s*′ plus the *chemical* five 3*d* orbitals (usually $3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$) then the point under discussion is not the same in the two procedures.

Nature of the Bonding.—The canonical molecular orbitals (CMO) (Table 3) are the solutions of the Roothaan–Hartree–Fock (RHF) equations and provide the best molecular energy *via* the variational freedom that they produce. It is possible to construct from these CMOs a set of localised bonds which do not alter either the total energy or the total electron density. There are circumstances where the CMOs are more relevant to the experimental data (*e.g.* in photoelectron spectroscopy) since each CMO has a unique energy; however, it is these localised molecular orbitals (LMO) which best fit the classical description of a chemical bond. We have therefore carried out the transformation to LMO by taking linear combinations of the valency shell CMOs such that the sum of the squares of the distances of the LMO centroids was maximised.[27,28] It is thus convenient to consider each method (CMO and LMO) of analysis of the bonding separately.

(a) *The delocalised* (*canonical*) *orbitals*. Although the present series of molecules (1a—c and e) contain varying numbers of electrons, there is a distinct similarity both between their molecular orbital types and those of naphthalene (Figure 2).[29] Thus the orbitals show a clear separation into those where the dominant eigenvectors indicate bonding parallel *or* perpendicular to the long molecular axis (L). Thus the orbital $7a_{1g}$ ($C_{10}H_8$, energy 18·80 eV) correlates with $16a_1$ [(1a), 20·21 eV],

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* Non-empirical calculations seem to reproduce experimental groupings satisfactorily in other conjugated heterocyclic systems, *e.g.* the azines [23] and azoles,[24] and when the known cross-sections for valency shell electrons are included in a line shape function, the experimental envelopes of intensity against energy in gas-phase XPS are reproduced.[21]

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[29] M. H. Palmer and S. M. F. Kennedy, following paper.

12a_1 [(1c), 21·08 eV], *etc.* as C + CH bonding parallel to the long axis. The highest orbital, bonding along the long axis and symmetrical to the short axis is 7b_{2u} ($C_{10}H_8$, 15·54 eV); in the pentalene derivatives this is destabilised, owing to the odd number of centres involved, in becoming the symmetrical lone pair orbital on sulphur [(1a), 8·49 eV] or oxygen [(1c), 11·78 eV].

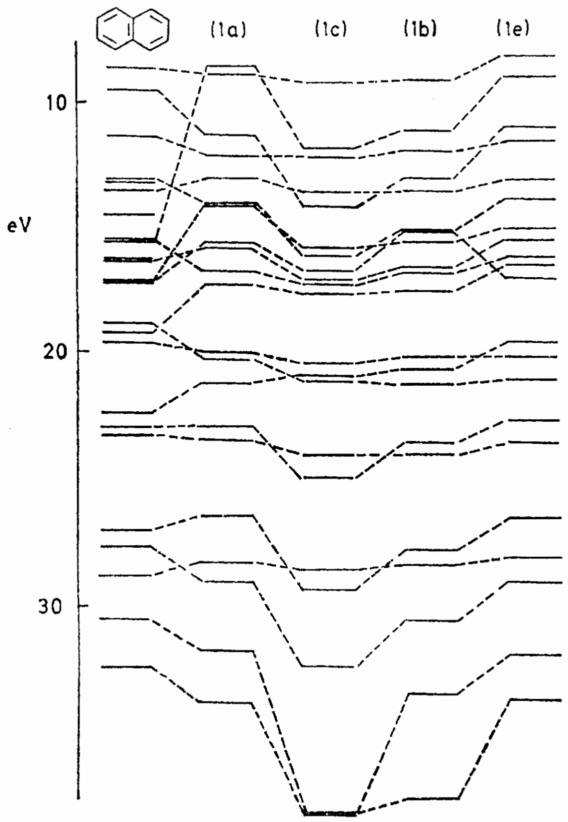

FIGURE 2 Correlation diagram for orbital energies (eV)

Most of the other principal changes in orbital ordering can be explained in terms of the orbital energies of the atoms contributing to the delocalised orbitals; relevant figures at the Hartree–Fock limit[30] are C_{2s} 19·20, C_{2p} 11·80; N_{2s} 25·72; N_{2p} 15·44; O_{2s} 33·86; O_{2p} 17·20; S_{3s} 23·94, S_{3p} 11·90 eV respectively.

(b) *Localised orbital description.* The LMO obtained (Table 4) were highly localised and were thus truncated, that is the remaining (small) fragments of other bonding centres were eliminated and the orbital *s*, *p*, *d* compositions re-normalised.[31] The σ/π separation was not enforced, and the general observation that LMOs favour two bent (' banana ') bonds over $\sigma + \pi$ was obtained.[32] Since these localised orbitals arise from the canonical orbitals, it is just as correct to regard these pairs of bent bonds as a $\sigma + \pi$ set.

Although we used the largest basis sets in these calculations for (1a, b, e; R = H) this choice will not significantly affect the nature of the localised orbitals for other basis sets since the *d* orbital contributions are so small. The C hybridisation in the C–H and C–C (single bond) orbitals is close to sp^2, while in those cases where bent bonds are formed the C hybrids in the C–X bond (X = C, N, or S) are close to sp^3 in all cases.[32] In contrast, the hybrid orbitals from C in the C–O bonds, and those from the N, O, and S atoms all have very high *p* orbital character; the *s* orbital components in the latter atoms are largely localised. As in the discussion of the delocalised orbitals, these conclusions are understandable in terms of the free atom orbital energies (above), with bond orbitals being formed mainly from atomic orbitals of similar energy and bonding hybrid orbitals occurring where the *s*/*p* orbital separation is smaller (C, 7·4; N, 10·28; O, 15·66; S, 12·04 eV).[30] Most of the bond orbitals are transferable within the series of molecules, since their kinetic energies are nearly constant for a given type; average values (a.u.) are C–H 1·186 ± 0·006 [C–H(O) excepted], C–C σ 1·609 ± 0·016 [C–C(O) excepted], C–C bent 1·425 ± 0·011, C(2,5)–S(1,6) 1·769 ± 0·002, C(3a)–S(6a) 1·801 ± 0·003. The lone pair orbitals on oxygen and sulphur have similar values to those in phosphoryl and thiophosphoryl halides.[28] In contrast the S(6)–S(6a) kinetic energy varies with the atom Y in (1): 1·930 (Y = S), 1·909 (Y = NH), 1·784 (Y = O). This is clear evidence of the change in bonding across the S–S–O system, and together with the disposition of the bent bond (σ/π) pairs is an indication of a strong tendency towards the classical formulation (2a; X = S, Y = O) with the nitrogen compound probably less so (kinetic energy high), and the S–S–S compound non-classical (1a). There is as yet insufficient data on the relative values of LMO kinetic energy and the factors which control it,* so that we are unable to determine from this method whether a bond exists at all between the S and O atoms. However the similarity in position of the two oxygen lone pair LMOs indicates that no S–O bond exists, and this is confirmed by the movement of the two S(6a) lone pair orbitals off the perpendicular plane through C(3a)–S(6a) and towards the O(1) side; that is, the system is adopting a dithiole electron configuration.

(c) *Conclusions on the nature of the bonding.* The similarity of much of the electronic structure to naphthalene is seen from the CMO picture, and it seems probable that the absence of aromatic character in these calculations of resonance energy is either that it does not exist in the form of that for naphthalene, or is obscured by the large amount of strain energy brought about by fusion of the two five-membered rings. The LMO picture clearly shows the change in bonding for (1) across the S–X, S–Y system with change in X and Y.

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* A relationship based upon the relative proportions of the bonding orbitals and their respective free atom energies would seem possible. Alternatively a relationship to the bond dissociation energies, after addition of the bond potential energy seems probable.

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TABLE 4

Valency shell localised orbitals

(*a*) Valency shell localised orbitals in 1,6,6a-trithiapentalene

Bonds/centres	Hybridisation (%)						Localisation	Position (Å)		Kinetic
A–B	*s*	*p*	*d*	*s*	*p*	*d*	degree (%)	A	B	energy/a.u.
C(2)–H	30·3	69·6					99·25	0·670	0·260	1·1873
C(3)–H	32·2	67·8					99·22	0·677	0·254	1·1875
C(2), C(3)σ/π	21·4	78·6		13·8	86·2		96·85	0·910	0·607	1·4200
C(3)C(3a)	23·8	76·2		32·8	67·3		98·51	0·694	0·724	1·6040
S(1)C(2)σ	7·4	87·6	5·0	27·8	72·2		99·11	0·896	0·798	1·7684
S(6a)C(3a)σ	10·5	84·2	5·3	30·4	69·6		98·37	0·907	0·817	1·8040
S(6a)S(1)	0·6	95·0	4·4	17·6	80·0	2·4	97·41	1·473	0·880	1·9298
S(1)(LP) σ	50·8	46·5	2·6	50·8	46·5	2·6	97·82	0·470		2·5106
S(1)C(2)(LP) [a] π	4·2	95·0	0·8	5·2	94·8		97·45	0·456	1·356	1·7623
S(6a) [b]	26·0	72·1	1·8		99·9		97·48	0·448	1·678	2·1254
S(6a)(LP) [c]	49·9	47·3	2·8				94·7	0·427		

[a] Nearly localised on S(1); principal eigenvectors given by: $0{\cdot}228\ (2p_\pi)_{1+6} - 0{\cdot}847\ (3p_\pi)_{1+6} - 0{\cdot}282\ (2p_\pi)_{2+5}$. [b] Nearly localised on S6(a); principal eigenvectors given by: $-0{\cdot}255(2s)_{6a} + 0{\cdot}498\ (3s)_{6a} + 0{\cdot}201\ (2p_\pi)_{6a} - 0{\cdot}195\ (2p_\sigma)_{6a} - 0{\cdot}751\ (3p_\pi)_{6a} - 0{\cdot}237\ (2p_\pi)_{3a}$. [c] $-0{\cdot}350\ (2s)_{6a} + 0{\cdot}711\ (3s)_{6a} - 0{\cdot}114\ (2p_\sigma)_{6a} + 0{\cdot}499\ (3p_\sigma)_{6a}$.

(*b*) Valency shell localised orbitals in 6,6a-dithia-1-azapentalene

Bonds/centres	Character (%)						Localisation	Position (Å)		Kinetic
	A			B						
A–B	*s*	*p*	*d*	*s*	*p*	*d*	degree (%)	A	B	energy/a.u.
C(2)–H	33·6	66·4		100			99·32	0·677	0·256	1·1850
C(3)–H	31·4	68·6		100			99·20	0·682	0·278	1·1805
C(4)–H	31·7	68·3		100			99·21	0·677	0·253	1·1838
C(5)–H	30·3	69·7		100			99·25	0·672	0·258	1·1846
N(1)–H	38·3	61·7		100			99·08	0·605	0·391	1·5304
C(2)–C(3)	26·5	73·5		24·7	75·3		98·43	0·676	0·694	1·6258
C(3)–C(3a) $\sigma + H$	12·1	87·9		25·4	74·6		95·87	0·602	0·970	1·4362
C(3a)–C(4)	30·9	69·1		24·4	75·6		98·47	0·697	0·721	1·6042
C(4)–C(5) $\sigma + \pi$	12·8	87·2		19·8	80·2		97·57	0·627	0·899	1·4230
C(2)–N(1) $\sigma + H$	18·6	81·4		14·9	85·1		98·90	0·933	0·705	1·6962
S(6a)–C(3a)	11·0	83·2	5·7	28·9	71·1		98·06	0·921	0·799	1·8179
S(6)–C(5)	6·9	87·7	5·3	28·0	72·0		99·14	0·908	0·770	1·7666
S(6)(LP)	46·6	51·0	2·4				97·70	0·460		2·4447
S(6)–S(6a)	16·7	80·9	2·4	0·5	94·2	5·3	97·72	0·883	1·470	1·9085
S(6)–C(LP) [a]	9·6	89·5	1·0	0·9	99·1		97·82	0·406	(1·498)	1·8729
S(6a)(LP) $\sigma + \pi$	36·4	61·4	2·2				85·83	0·450		2·3248
N–S(LP) [b]	42·8	57·2		0·7	94·2	5·1	97·11	0·618	(1·468)	1·9799

(*c*) Valency shell localised orbitals in 1-oxa-6,6a-dithiapentalene

Bonds/centres	Character (%)						Localisation	Position (Å)		Kinetic
	A			B						
A–B	*s*	*p*	*d*	*s*	*p*	*d*	degree (%)	A	B	energy (a.u.)
C(2)–H	31·6	68·4		100			98·89	0·682	0·248	1·2035
C(3)–H	31·8	68·1		100			99·22	0·679	0·252	1·1840
C(4)–H	31·9	68·1		100			99·20	0·674	0·257	1·1901
C(5)–H	30·9	69·1		100			99·28	0·665	0·266	1·1893
C(2)–C(3)	29·4	70·6		25·3	74·7		98·21	0·686	0·683	1·6510
C(3)–C(3a) $\sigma + \pi$	11·5	88·5		23·3	76·7		97·16	0·653	0·912	1·4305
C(3)–C(4)	31·0	69·0		25·1	74·9		98·44	0·694	0·724	1·6017
C(4)–C(5) $\sigma + \pi$	12·9	87·1		18·9	81·1		98·13	0·664	0·859	1·4219
O(1)–C(2) $\sigma + \pi$	11·0	89·0		15·2	84·8		99·41	0·549	0·849	1·9930
S(6a)–C(3a)	9·1	85·6	5·4	28·3	71·7		98·53	0·918	0·801	1·7823
S(6)–C(5)	7·1	87·2	5·7	26·9	73·1		99·06	0·907	0·763	1·7708
S(6)–S(6a)	11·6	85·9	2·5	4·8	92·2	3·0	98·48	1·063	1·289	1·7835
O(1)(LP)	47·7	52·3					98·37	0·309		2·9582
O(1)(LP)	36·2	63·8					98·02	0·384		2·7122
S(6a)(LP) $\sigma + \pi$	34·0	64·0	2·0				97·19	0·470		2·2967
S(6)(LP) $\sigma + \pi$	30·5	67·7	1·8				97·71	0·450		2·2168

[a] Nearly localised on sulphur (see text); principal eigenvectors given by: $0{\cdot}300\ (3s)_6 - 0{\cdot}847\ (3p)_6 - 0{\cdot}238\ (2p)_5 + 0{\cdot}227\ (2p)_6$.
[b] Nearly localised on nitrogen (see text); principal eigenvectors given by: $-0{\cdot}577\ (2s)_1 + 0{\cdot}630\ (2p_x)_1 - 0{\cdot}340\ (3p_x)_{6a}$.

Thus for (1a), two S–S bonds exist; for (1e) the S–N bond is weak, while in (1b) the S–O bond is absent and the molecule is best represented as (2a; X = S, Y = O). The occurrence of two lone pair orbitals at S(6a) in (1a; X = Y = S) is indicative of an overall trigonal bipyramid structure for S(6a); although it is conventional to invoke extensive 3*d* orbital participation to account for this, it is worth noting that in ClF_3, recent calculations,[33] similar in nature to the present work, have shown that the 3*d* orbital population is not essential to the bonding scheme. We are thus likely to see a range of levels of 3*d* orbital participation in compounds of second row elements. Here (1a) the level is particularly low, and this may in part result from the cyclic system allowing other routes for the interchange of electron density between the centres.

APPENDIX

The molecular binding energy (and total energy) is numerically large and gives comparatively little information concerning the stability of the molecule (except to atomisation) and does not give any real indication of properties like aromatic character. The concept of resonance energy has usually been based upon thermochemical data or empirical calculations. In the present method, the total energy of a sequence of molecules which contain fragments of the classical structures of (1a—e) were determined and this enables an estimate of the resonance energy of the molecule [*e.g.* (1a)] to be obtained by difference between the molecular energy of (1a) and the sum of the fragments.

The procedure is based upon the determination of C–H, C–C, C=C, C–S, and C=S bond energies. Thus the total energy of methane ($E_{CH_4} = -40{\cdot}10325$ a.u.) yields the energy of the C–H bond ($E_{CH} = \frac{1}{4}E_{CH_4} = -10{\cdot}02581$ a.u.); insertion of this value into the ethylene molecule ($E_{C_2H_4} = E_{C=C} + 4E_{CH} = -77{\cdot}83143$ a.u.) yields $E_{C=C} = -37{\cdot}72818$ a.u. Similar procedures with a twisted molecule of buta-1,3-diene (where the π-orbitals are perpendicular to each other) yields $E_{C-C} = -18{\cdot}89797$ a.u. for C_{sp^2}–C_{sp^2}. Other molecules necessary for the present work, and the bond energies (a.u.) obtained, are: CH_2=CHOH ($E_{C-O} = -46{\cdot}7451$), CH_2=CHSH ($E_{C-S}{}^{sp} = -207{\cdot}78481$, $E_{C-S}{}^{spd} = -207{\cdot}8391$) both these molecules have the X–H (X = O or S) bond out-of-plane; H_2O ($E_{OH} = -37{\cdot}8999$); NH_3 ($E_{NH} = -18{\cdot}6733$); H_2S ($E_{SH}{}^{sp} = -198{\cdot}9221$, $E_{SH}{}^{spd} = -198{\cdot}9702$); CH_2O ($E_{C=O} = -93{\cdot}4592$); CH_2S ($E_{C=S}{}^{sp} = -415{\cdot}5437$, $E_{C=S}{}^{spd} = -415{\cdot}6309$); H_2S_2 ($E_{S-S}{}^{sp} = -396{\cdot}7094$, $E_{S-S}{}^{spd} = -396{\cdot}8172$); HOSH ($E_{O-S}{}^{sp} = -235{\cdot}6416$, $E_{O-S}{}^{spd} = -235{\cdot}6923$); $HSNH_2$ ($E_{S-N}{}^{sp} = -216{\cdot}4159$; $E_{S-N}{}^{spd} = -216{\cdot}4655$). All the calculations were run using the experimental geometry where known, and others were derived from known bond lengths and angles. Most *importantly*, all the calculations used *identical* basis sets for the atoms to those of the main work in this paper. Work with other basis sets showed that the resonance energies are reproducible to within 10% for selected molecules (*e.g.* benzene and pyrrole).

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[33] A. Breeze, D. W. J. Cruickshank, and D. R. Armstrong, *J.C.S. Faraday II*, 1972, 2144.