

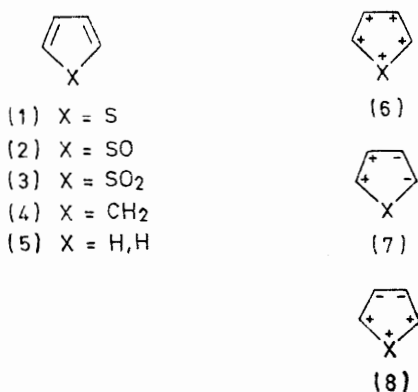
Non-empirical Calculations of the Nature of the Bonding in Thiophen, Thiophen S-Oxide, and Thiophen SS-Dioxide

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LCGO Calculations are reported for the title compounds. A non-planar structure similar to that recently reported for 1-benzylphosphole is more stable than the planar form for the S-oxide. The electron distributions are interpreted in terms of localised orbitals, and it is clear that the 3d orbitals play a significant part in the bonding of the S-oxide and SS-dioxide. Neither of the latter compounds show evidence of aromatic character; the overlap populations show a progressive increase in diene character across the series pyrrole, thiophen, its S-oxide, and its SS-dioxide, consistent with the ready dimerisation of the latter pair.

In previous papers we reported non-empirical MO calculations of the electronic structure of five and six-membered ring heterocycles,¹⁻⁵ containing oxygen and/or nitrogen. More recently this was extended to studies of heterocycles containing phosphorus and sulphur.⁶⁻⁸ A feature of much of this work, and now a matter of policy, is to use a standardised basis set,⁶⁻⁹ such that the results for various molecules are comparable and small differences in electronic structure may become evident.

The principal objectives of the present work are to compare and contrast thiophen (1) with its S-oxide (2)



and SS-dioxide (3). Following the observation that 1-benzylphosphole has both P and 1-CH₂ out of the hydrocarbon plane,¹⁰ we have attempted to find the geometry

¹ M. H. Palmer and A. J. Gaskell, *Theor. Chim. Acta*, 1971, **23**, 52.

² M. H. Palmer, A. J. Gaskell, and M. S. Barber, *J. Mol. Struct.*, 1972, **12**, 197.

³ M. H. Palmer, A. J. Gaskell, and R. H. Findlay, *J.C.S. Perkin II*, 1974, 778.

⁴ S. Craddock, R. H. Findlay, and M. H. Palmer, *Tetrahedron*, 1973, **29**, 2173.

⁵ M. H. Palmer, R. H. Findlay, and A. J. Gaskell, *J.C.S. Perkin II*, 1974, 420.

⁶ M. H. Palmer and R. H. Findlay, *Tetrahedron Letters*, 1972, 4165.

⁷ M. H. Palmer and R. H. Findlay, *J.C.S. Perkin II*, 1974, 1885.

⁸ M. H. Palmer and S. M. F. Kennedy, *J.C.S. Perkin II*, 1974, 1893.

⁹ M. H. Palmer, A. J. Gaskell, and M. S. Barber, *Theor. Chim. Acta*, 1972, **26**, 357.

¹⁰ P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quinn, *J. Amer. Chem. Soc.*, 1970, **92**, 5779.

around the S atom in both the S-oxide (2) or SS-dioxide (3); we comment upon the low inversion barrier in some thiophen S-oxides.^{11,12} The study reports the effect of the 3d_S orbitals on the bonding in (2) and (3), which are compared with earlier theoretical¹³⁻¹⁵ and photoelectron spectroscopic studies of aliphatic sulphoxides and sulphones.¹⁶⁻¹⁸ Finally, in contrast to thiophen which is extremely stable,¹⁹ thiophen S-oxide (2) undergoes rapid dimerisation¹¹ and we investigate reasons for this difference.

METHODS

The Orbital Basis.—The linear combination of gaussian orbital (LCGO) procedure was used, and each orbital was represented by a series of gaussian type functions (GTFs) identical with those used previously.^{6-9,20} Briefly, the orbitals 1s_H, 1s_M, 2s_M, and 2p_M (M = C or O) were represented by 3, 5, 2, and 3 s- or p-type GTFs respectively, while the sulphur atom was represented by 6(1s), 2(2s), 2(3s), 4(2p), 2(3p), and 1(3d) GTFs. As usual in LCGO studies it is necessary to use six 3d functions (of types 3d_A where A = xy, xz, yz, x², y², z²) in order to preserve the three-fold symmetry of the indices during evaluation of the electron repulsion integrals. This set of six 3d_A functions were converted, by taking linear combinations,²¹ into the usual 'chemical set' with A = xy, xz, yz, x² - y², and z², and a further s orbital (3s¹) corresponding to A = x² + y² + z² = r². In the following discussion only the group of five are referred to as the 3d orbitals. In order to study the effect of these and of the 3s¹ function, various combinations were used in the self-consistent field stage of the calculation after integral evaluation.

¹¹ W. L. Mock, *J. Amer. Chem. Soc.*, 1970, **92**, 7610.

¹² D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4854.

¹³ W. Moffitt, *Proc. Roy. Soc.*, 1950, **A**, **200**, 409.

¹⁴ G. L. Bendazzoli, F. Bernardi, P. Palmieri, and C. Zauli, *J. Chem. Soc. (A)*, 1968, 2186.

¹⁵ A. D. Walsh, *J. Chem. Soc.*, 1953, 2306.

¹⁶ G. W. Mines, R. K. Thomas, and H. Thompson, *Proc. Roy. Soc.*, 1972, **A**, **329**, 275.

¹⁷ H. Bock and B. Solouki, *Angew. Chem. Internat. Edn.*, 1972, **11**, 436.

¹⁸ B. Solouki, H. Bock, and R. Appel, *Angew. Chem. Internat. Edn.*, 1972, **11**, 927.

¹⁹ M. H. Palmer, 'Structure and Reactions of Heterocyclic Compounds', Arnold, London, 1967.

²⁰ M. H. Palmer and R. H. Findlay, *J.C.S. Perkin II*, 1975, 841.

²¹ A. Rauk and I. G. Csizmadia, *Canad. J. Chem.*, 1968, **46**, 1205.

The Gaussian Exponents.—The exponents used had earlier been optimised so as to produce the best free atom energy consistent with the number of functions used,¹ and these 'best atom' energies (with the corresponding Hartree-Fock limiting values in parentheses) are H(2s) -0.4971 (-0.5000), C(2p) -37.6106 (-37.6886), O(2p) -74.6121 (-74.8090), and S(3p) -396.6988 (-397.5050) a.u. respectively. As can be seen these functions obtain $>99.7\%$ of the Hartree-Fock free atom energies.²³ In the second stage further optimisation of the exponents was done to allow for the molecular environment, by means of studies of the energy surface against orbital exponents, as described earlier for C and H.⁹ It was extended to sulphur by similar studies on CH₂S, which also allowed optimisation of the 3d_s exponent (the 3d_s orbitals are vacant in the free atom). The best total energy was -435.68175 a.u. (*spd* + 3s¹ basis) or -435.59460 a.u. (*sp* basis) to be compared with an earlier calculation,²³ -431.74468 a.u.; the latter is clearly an

relative to the hydrocarbon plane (*cf.* 1-benzylphosphole¹⁰) and the angle (θ) between the SO bond and C(2)SC(5) plane.

RESULTS AND DISCUSSION

Geometry of the SS-Dioxide (3) and the S-Oxide (2).—Parabolic minimisation of the total energy as a function of OSO angle gave the following results as a function of basis set: *sp*, 100.3°; *sp* + 3s¹, 116.3°; *spd*, 118.5°; *spd* + 3s¹, 118.5°. Since at all angles in the range 40–135° the total energy is lowered in the order *sp* + 3s¹ < *spd* < *spd* + 3s¹, it is clear that the *sp* basis is less reliable than the others in predicting the equilibrium geometry. Thus an OSO angle of *ca.* 118° seems probable, and this is consistent with dibenzothiophen SS-dioxide (120.0°)²⁶ and tetrahydrothiophen SS-dioxide (117.8°),²⁷ showing that the aromatic character of the

TABLE I
Molecular energy of thiophen SS-dioxide as a function of basis set and geometry.

	Basis set			
	<i>sp</i>	<i>sp</i> + 3s ¹	<i>spd</i>	<i>spd</i> + 3s ¹
OSO 120°				
Total energy (a.u.)	-698.904 00	-698.958 27	-699.255 19	-699.305 79
Binding energy (a.u.)	-0.550 16	-0.604 44	-0.901 36	-0.952 00
Relative energy (kJ mol ⁻¹)	0.0	-143	-922	-1 055
OSO 80°				
Relative energy (kJ mol ⁻¹)	+251	+110	-579	-710
OSO 135°				
Relative energy (kJ mol ⁻¹)	+257	+120	-678	-807

inadequate basis, and this is also apparent from the *low* calculated first ionisation potential (IP) (8.32 eV). The Hartree-Fock procedure when carried out with an adequate basis must yield a numerical value theoretical \geq experiment (9.44 eV);²⁴ the present work yields values in the range of 9.40–9.62 eV (*sp*, *spd* + 3s¹ basis).

Geometric Features.—Thiophen was studied at the experimental geometry.²⁵ For the S-oxide (2) and SS-dioxide (3), iterative cycling by the CNDO/2 method with variation in the C(2)–C(3) bond length and parabolic minimisation of the total energy led to optimum lengths of 1.334 and 1.332 Å respectively, to be compared with 1.371 Å in thiophen. The variation in length is very small, and the energy surface in the following LCGO calculations would be prohibitively expensive to explore for C(2)–C(3) variation. Thus the ring geometry for (2) and (3) was fixed as in (1); for the SS-dioxide (3) the SO length (1.49 Å) was chosen as for dibenzothiophen SS-dioxide,²⁶ and the OSO angle was varied between 40 and 135°, and the optimum value determined for each basis set by parabolic minimisation of the total energy against angle. For the S-oxide (2) a similar series of parabolic minimisations was employed with simultaneous variation of the out-of-plane height (*h*) of the sulphur atom

thiophen ring has little effect upon the geometry. The question of whether the SS-dioxide (3) itself has any aromatic character is discussed below. Since the optimum angle lies close to one of the selected angles 120°, redetermination of the molecular energies and populations are not warranted, and in the Tables we record the data for the 120° result. The lowering of the total energy (the energy relative to the 120° *sp* basis calculation in Table I) shows that a single 3s¹ function lowers the energy by *ca.* 140 kJ mol⁻¹ for all geometries, while the five 3d orbitals have a lowering of *ca.* 800 kJ mol⁻¹, more than a proportional effect. As can be seen from the population analyses below the SO bonds are very polar, and the 3s¹–3d functions provide a mechanism for reduction of this polarity.

In the first attempt at optimisation of the S-oxide geometry the thiophen part of the ring was held constant, and only the oxygen atom varied out of plane. The optimum angle (θ) between the C(2)SC(5) plane and the SO bond as a function of basis set was *sp*, 142.7°; *sp* + 3s¹, 142.3°; *spd*, 134.3°; *spd* + 3s¹, 134.1°. Thus in the SS-dioxide studies (a) the 3d orbitals have a comparatively small additional effect over the 3s¹ orbital and (b) the *sp* basis alone largely determines the

²² E. Clementi, *I.B.M. J. Res. Development*, 1965, **9**, 2.

²³ N. C. Baird and J. R. Swenson, *J. Phys. Chem.*, 1973, **77**, 277.

²⁴ A. Jones and F. P. Lossing, *J. Phys. Chem.*, 1967, **71**, 4111.

²⁵ B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1961, **7**, 58.

²⁶ L. Kronfield and R. L. Sass, *Acta Cryst.*, 1968, **24**, 981.

²⁷ F. Ellis, P. G. Sammes, M. B. Hurthouse, and S. Neidle, *J.C.S. Perkin I*, 1972, 1560.

geometry. When both sulphur and oxygen was allowed to move out-of-plane the following values for the out-of-plane distance (h) and the angle (θ) were sp , h 0.16 Å, θ 138.9°; $sp + 3s^1$, h 0.25 Å, θ 138.6°; spd , h 0.23 Å, θ 134.2°; $spd + 3s^1$, h 0.23 Å, θ 134.1°. Again the energy is lowered by the addition of the $3d$ orbitals for all geometries (Table 2), but the effect (*ca.* 470 kJ mol⁻¹) is only about half that in the SS-dioxide. Overall it is clear that the $3d$ orbitals have a significant bonding role as in the SS-dioxide, but again the geometry is *largely* determined by the sp basis alone. Taking the results of the largest basis set, the optimum out-of-plane movement of S in the S-oxide must be near 0.23 Å and not significantly different from that for phosphorus in 1-benzylphosphole (0.21 Å);¹⁰ the angle θ is however

S-oxide than in the other compounds including 1-benzylphosphole (θ 113°); this may well be associated with the aromatic character of the thiophen ring (see below).†

Inversion Barrier of S-Oxide.—If we take the energy difference between the optimal pyramidal form and the planar form of the S-oxide (2) as the inversion barrier we obtain a value varying from 16 (sp basis) to 44 kJ mol⁻¹ ($spd + 3s^1$). In view of the significant role of the $3d$ orbitals in both lowering the total energy (above) and stabilising some of the molecular orbitals (below), it is appropriate to take a value near the maximum of this range. The only experimental value¹¹ to date refers to 2,5-bis-(2,2-dimethylhexyl)thiophen S-oxide, for which the barrier is 62 kJ mol⁻¹. The two values are of similar order of magnitude, and it seems probable that the

TABLE 2

Molecular energies for thiophen S-oxides at selected geometries for all basis sets

	Basis set			
	sp	$sp + 3s^1$	spd	$spd + 3s^1$
Planar				
Total energy (a.u.) ^{a,b}	-0.468 93	-0.519 56	-0.641 67	-0.690 87
Binding energy (a.u.)	-0.727 80	-0.778 43	-0.900 54	-0.949 74
Relative energy (kJ mol ⁻¹)	0.0	0.0	0.0	0.0
O Out of plane (140°) ^c				
Total energy (a.u.) ^{a,b}	-0.474 52	-0.525 19	-0.654 72	-0.070 81
Binding energy (a.u.)	-0.733 39	-0.784 06	-0.913 59	-0.962 68
Relative energy (kJ mol ⁻¹)	0.0	133	473	602
S,O Out of plane (h 0.2; θ 135°) ^d				
Total energy (a.u.) ^{a,b}	-0.474 93	-0.525 76	-0.658 58	-0.707 78
Binding energy (a.u.)	-0.733 80	-0.784 63	-0.917 45	-0.966 65
Relative energy	0.0	133	482	611
Inversion barrier (kJ mol ⁻¹)	15.8	16.3	44.4	44.4

^a Relative to -624.000 00 a.u. ^b 1 a.u. = 627.5 kcal mol⁻¹ = 2 626.0 kJ mol⁻¹. ^c Angle between hydrocarbon plane and SO bond. ^d Height of S atom above C(2)C(3)C(4)C(5) plane, h ; angle between C(2)SC(5) plane and SO bond, θ (see text).

rather larger in the S-oxide, showing that the sulphur atom prefers a rather more flat pyramid than phosphorus in 1-benzylphosphole. In view of the differing CS and CP bond lengths however, more realistic comparisons in the first instance are between dimethyl sulphoxide and thiophen S-oxide; under these conditions the variables h and θ chosen for computational simplicity are better replaced by the C(2)C(5) pyramid height l and the angle θ between the C(2)SC(5) plane and the SO bond. The results based upon the microwave spectrum for dimethyl sulphoxide,²⁸ thionyl fluoride,²⁹ and the optimal thiophen S-oxide geometry are Me₂SO: l 0.71 Å, θ 115.6°; * F₂SO: θ 114.8°; C₄H₄SO: l 0.54 Å, θ 138.9° (sp basis); C₄H₄SO: l 0.54 Å, θ 134.0° ($spd + 3s^1$ basis). There are no data on conjugated sulphoxides, but it is clear that the pyramid angle θ is much larger in thiophen

present work would reproduce the much higher value for aliphatic or aryl sulphoxides (150–170 kJ mol⁻¹)^{12,32} as it does between phosphines and phospholes. It has been proposed that the low barrier in the thiophen S-oxide (above) and in phospholes arises from stabilisation of the transition state for inversion owing to the aromatic character of the thiophen (or phosphole) system.^{11,32} If the planar S-oxide was aromatic, *i.e.* had an energy lower than the classical bond energy sum, then it would be the ground state rather than a transition state energy maximum, by the same reasoning that we recently applied to phosphole. An alternative explanation for the low barrier can be based upon a valency force field; the potential function in equation (1) has been widely applied to inversion barriers, and gives a satisfactory

* The recent statement³⁰ that the angle θ is 122° 47', and based upon the data of ref. 27 is incorrect.

† Strain in the five-membered ring system seems unlikely to account for these differences, since the CSC angles in dimethyl sulphide and sulphoxide differ^{28,31} by only 2.5°, and hence the use of the same angle in S-oxide (2) and thiophen is a reasonable approximation.

²⁸ H. Von Dreizler and G. Dendl, *Z. Naturforsch.*, 1964, **19a**, 512.

²⁹ R. C. Ferguson, *J. Amer. Chem. Soc.*, 1954, **76**, 850.

³⁰ J. W. Bevan, A. C. Legon, and D. J. Millen, *J.C.S. Chem. Comm.*, 1974, 659.

³¹ L. Pierce and M. Hayashi, *J. Chem. Phys.*, 1961, **35**, 479.

³² A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6507.

account of many variations in barriers.³³ The equation relates the stretching and bending force constants (k_l and k_b), the changes in length (Δl) of the XY bond, and angle ($\Delta\alpha$) of the YXY angle in XY_3 , to the energy change. If no changes in length are assumed then equation (2) is relevant, while if a cyclic system is involved such that one angle remains unchanged, then (2) is replaced by (3).³³

$$V_i = \frac{2}{3}[K_l(\Delta l)^2 + K_b(\Delta\alpha)^2] \quad (1)$$

$$V_i = K(\Delta\alpha)^2 \quad (2)$$

$$V_\alpha = \frac{2}{3}K(\Delta\alpha)^2 \quad (3)$$

The angle changes are from 119.9 to 134° in thiophen S-oxide, and 106 to 120° (approximately) in planar dimethyl sulphoxide, using the assumption that the ring

barrier for the cyclic system is explained directly by the requirement of the ring system to retain one angle largely constant. On this basis cyclic systems with small rings should always show smaller inversion barriers to corresponding acyclic types *unless* the pyramid angle is so different that $\Delta\alpha$ varies significantly between the two systems. Such an occurrence is seen in aziridines.^{33b}

Overall Nature of the Bonding and Electron Distribution.—We noted above that introduction of $3s^1$ and $3d$ orbitals to sulphur lowers the molecular energy; in general in all non-empirical calculations the addition of basis functions to centres will lead to a lowering of the molecular total energy towards the Hartree-Fock single configuration limit.³⁴ This lowering occurs through additional variational freedom given by the added functions. Now in the Hartree-Fock theory the molecular total energy is the sum of the orbital energies (ϵ_i),

TABLE 3
Orbital energies for thiophen, its S-oxide, and SS-dioxide (eV)

Basis	Thiophen		Planar S-oxide		Pyramidal S-oxide		SS-Dioxide	
	sp	$spd + 3s^1$	sp	$spd + 3s^1$	sp	$spd + 3s^1$	sp	$spd + 3s^1$
a_1	a_1	a_1	a_1	a_1	a^1	a^1	a_1	a_1
-2 492	-2 495	-2 498	-2 501	-2 498	-2 498	-2 500	-2 503	-2 505
-307.3	-307.1	-554.7	-558.0	-553.6	-556.3	-554.4	-557.6	
-307.0	-306.7	-308.1	-308.0	-308.1	-307.9	-309.3	-309.0	
-237.5	-237.9	-307.8	-307.4	-307.9	-307.7	-308.4	-308.2	
-179.8	-180.4	-242.5	-242.6	-242.4	-242.1	-247.1	-246.1	
-32.64	-32.07	-185.1	-185.4	-184.9	-184.9	-189.6	-188.9	
-26.96	-26.61	-36.36	-37.22	-184.7	-184.7	-39.34	-38.94	
-20.92	-20.75	-33.11	-32.65	-36.28	-36.48	-33.76	-33.28	
-19.51	-19.26	-27.40	-26.94	-32.96	-32.68	-27.73	-27.13	
-15.36	-15.21	-21.51	-21.26	-27.27	-26.88	-22.23	-21.90	
-12.99	-13.17	-19.94	-19.97	-21.57	-21.37	-20.84	-20.54	
b_2	b_2	-16.03	-15.95	-20.15	-19.93	-17.40	-17.71	
-307.3	-307.1	-14.74	-15.52	-17.11	-16.79	-17.07	-16.75	
-307.0	-306.7	b_2	b_2	-16.18	-15.99	-11.33	-12.97	
-179.8	-180.4	-308.1	-308.0	-14.94	-15.38	b_2	b_2	
-27.06	-26.80	-307.8	-307.4	-17.98	-13.37	-309.3	-309.0	
-20.53	-20.37	-185.0	-185.3	-9.32	-9.77	-308.4	-308.2	
-16.25	-15.95	-27.90	-27.60	a^{11}	a^{11}	-189.5	-188.8	
-14.67	-16.42	-21.63	-21.32	-308.1	-307.9	-28.94	-28.50	
b_1	b_1	-17.10	-16.80	-307.9	-307.7	-23.08	+22.53	
-179.7	-180.7	-16.50	-16.30	-184.8	-184.8	-18.25	-17.84	
-15.30	-14.96	-11.24	-12.73	-27.98	-27.73	-17.78	-17.40	
-10.25	-9.91	b_1	b_1	-21.67	-21.42	b_1	b_1	
a_2	a_2	-184.8	-185.3	-17.11	-16.82	-554.4	-557.7	
-9.82	-9.51	-17.36	-17.10	-16.55	-16.37	-189.6	-188.9	
		-13.82	-14.23	-10.87	-11.87	-35.18	-35.67	
		-9.05	-9.26	-10.38	-10.22	-17.04	-17.11	
		a_2	a_2			-14.01	-14.41	
		-10.61	-10.30			-11.20	-12.08	
						a_2	a_2	
						-12.51	-13.60	
						-10.93	-10.54	

angle remains unchanged and the CSC and CSO angles in dimethyl sulphoxide are equal. Thus the ratio of energies is given by $\frac{2}{3}(k_1/k_2)$ where k_1 and k_2 are the force constant for the cyclic and acyclic systems respectively. Since the force constants are unlikely to vary markedly for similar elements^{33b} the diminution in the inversion

the one-electron energies, and the nuclear repulsion. For adequate basis sets, the orbital energies are numerically equal to or greater than the corresponding ionisation potential (IP), when Koopmans' theorem is used.³⁴ Polarisation functions reduce the discrepancy between the observed IP_i and $-\epsilon_i$, i.e. they lower the orbital binding energy. In contrast, in the LCAO method, we understand a bonding function to arise from mixing of

³³ (a) R. E. Weston, *J. Amer. Chem. Soc.*, 1954, **76**, 2645; (b) G. W. Koepl, D. S. Sagatys, G. S. Krishnamurthy, and S. L. Miller, *ibid.*, 1967, **89**, 3396; (c) C. C. Costain and G. B. B. M. Sutherland, *J. Phys. Chem.*, 1952, **56**, 321.

³⁴ W. G. Richards and J. A. Horsley, 'Ab Initio Molecular Orbital Calculations for Chemists,' Clarendon, Oxford, 1970.

atomic orbitals with a resultant lowering of the MO energy below that of the constituent AOs.

In our earlier work⁶⁻⁸ with sulphur heterocycles we noted in various formally covalent S compounds such as (1), the dithiolium cations, and even thiathiophthens that the role of the $3d_s$ orbitals was that of polarisation functions. As can be seen from Table 3, this is not the case for the S-oxide (2) and SS-dioxide (3), where some of the orbital energies are stabilised by the addition of $3d_s$ functions. For the present molecules, the delocalised orbitals show additional complex features arising from the highly polar SO and SO₂ groupings, and we discuss these individual orbitals after consideration of the overall

localised fragments are eliminated and the LMOs are re-normalised yielding the $sp(d)$ character shown. It is emphasised that there is *no* change in electron density in this procedure and thus the two descriptions are entirely equivalent. In the following discussion the largest ($spd + 3s$) basis sets were used for (1)–(3); the results concerning the nature of the bonding are unlikely to be changed markedly by change of basis since the $3d_s$ and $3s^1_s$ components are relatively small. For thiophen the localisation procedure was carried out in three ways; (a) allowing σ - π mixing [as occurs in non-planar (2)], (b) σ localised and π remaining delocalised, and (c) localisation of the π -MOs following (b). In all three cases the

TABLE 4
Valency shell localised orbitals

Bond-centres A-B	Character (%)				Location degree (%)	Position (Å)		Kinetic energy (a.u.)
	s	A p	d	B s		A	B	
(a) Thiophen								
C(2)-H	35.0	65.0		100	99.27	0.728	0.350	1.1267
C(3)-H	32.7	67.3		100	99.28	0.733	0.348	1.080
C(2)-C(3) σ	34.4	65.6		29.4	70.6	0.675	0.696	1.6506
C(2)-C(3) π		100.0			100.0	0.731	0.654	1.1963
C(3)-C(4)	28.2	71.8		28.2	71.8	0.714	0.714	1.5765
S-C(2)	26.2	69.6	4.2	26.2	73.8	0.907	0.810	1.8552
S _{LP} (π)		99.8	0.2			0.220		1.7495
S _{LP} (σ)	63.0	36.9	0.0			0.518		2.7638
C(2)-C(3) σ - π	18.0	82.0		15.4	84.6	0.774	0.751	1.4325
(b) Thiophen S-oxide								
C(2)-H	35.3	64.7		100	99.27	0.722	0.357	1.1315
C(3)-H	33.4	66.6		100	99.28	0.727	0.354	1.1182
C(2)-C(3) σ - π '	17.9	82.1		15.3	85.7	0.775	0.747	1.4291
C(3)-C(4)	27.9	72.1		27.9	72.1	0.714	0.714	1.5712
S-C(2)	14.3	78.8		26.5	73.5	0.912	0.820	1.8254
S=O	19.1	68.9	12.0	3.5	96.5	1.118	0.496	2.2486
S _{LP} ' π '	22.7	75.7	1.6			0.484		2.1163
O _{LP}	50.0	50.0				0.282		2.9547
O _{LP} ' π '	48.5	51.5				0.280		2.9435
(c) Thiophen SS-dioxide								
C(2)-H	35.2	64.8		100	99.28	0.717	0.361	1.1325
C(3)-H	32.9	67.1		100	99.26	0.725	0.356	1.1243
C(2)-C(3) σ - π	16.4	83.6		16.0	84.0	0.748	0.780	1.4281
C(3)-C(4)	27.7	72.3		27.7	72.3	0.714	0.714	1.5734
S-C(2)	20.2	70.0	9.8	27.3	72.7	0.952	0.765	1.9051
S=O	23.3	65.3	11.4	2.6	97.4	1.044	0.537	2.2732
S=O	7.05	70.6	22.3	10.9	89.1	1.221	0.438	2.2990
(O _{LP}) ₂	54.7	45.3				0.252		2.9903
(O _{LP}) ₂	51.7	48.3				0.256		2.7443

electron distribution. A system of largely localised bonds (Table 4) can be produced by a unitary transformation which does not change *either* the total energy *or* the total electron density at any point. As previously⁷ we took linear combinations of the valency shell canonical orbitals, such that the sum of the squares of the distances between the localised orbital (LMO) centroids was maximised.³⁵ It is usually not possible to achieve complete localisation (see Table 4) and conventionally the orbitals are then truncated,³⁶ that is the remaining non-

total kinetic energy is unchanged, and the sum of the ($\sigma + \pi$) C(2)C(3) kinetic energies is equal to the pair of 'banana' (bent) bonds formed when (a) was followed.^{7,37} The kinetic energy of the σ -bond is slightly different for C(2)C(3) than C(3)C(4). In method (c) the σ -lone pair on sulphur shows a high $3s_s$ character, while the π -lone pair of pure $3p_s$ character is displaced *towards* the C(2) and C(5) atoms by 0.22 Å, a sign of delocalisation into the ring. For the S-oxide (2) and SS-dioxide (3) σ - π mixing was allowed so that in Table 4 we include the relevant data for methods (a) and (c) for thiophen.

³⁵ M. F. Guest, I. H. Hillier, and V. R. Saunders, *J.C.S. Faraday II*, 1972, 867.

³⁶ E. Switkes, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, 1969, **51**, 2085; E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, 1970, **92**, 3847.

³⁷ C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, 1965, **43**, S97; U. Kaldor, *ibid.*, 1967, **46**, 1981; M. D. Newton, E. Switkes, and W. N. Lipscomb, *ibid.*, 1970, **53**, 2645; M. D. Newton and E. Switkes, *ibid.*, 1971, **54**, 3179.

The *S*-oxide (2) shows two bent SO bonds which lie roughly parallel to the hydrocarbon plane, and which in the planar form would both lie in the σ -system. This view is consistent with earlier theoretical notions,^{13,15} and draws a clear distinction with, for example cyclopentadienone where the π -system extends to oxygen. The sulphur atom in (2) carries a lone pair, largely of $3p_S$ character, which mixes with the hydrocarbon π -system, and which is related to the third π -level ($3b_1$) in thiophen. Consistent with this is the distortion of this lone pair towards the ring; thus the orbital lies on an axis of 28° from the external bisector of the C(2)C(5)SO pyramid external angle at S, and towards the ring. Furthermore the kinetic energy of this lone pair is markedly different from the central lone pair in S₂O (2.9402 a.u.) where it is effectively non-interacting with the adjacent S=S and

plane containing SO₂, rather than transverse to the same plane in the *S*-oxide (2). Furthermore in each bond, one orbital is of much higher $2p_O$ - $3p_S$ character; thus we can again separate these into two orbitals in each bond, one of π -symmetry with respect to the SO axis, the other of σ -symmetry.¹³ The oxygen lone pairs are antisymmetric with respect to the SO₂ plane, and of course slightly non-equivalent owing to the bent SO₂ system.

Comparison of the centroid positions in the bond A-B with covalent radii for the atoms concerned gives an estimate of the bond polarisation. Relevant figures (Å) are H, 0.28–0.37; C, 0.77; S, 1.04; and O, 0.66. Some non-additivity must be expected in view of the assumptions made in deriving such radii. It is clear that irrespective of the value for H, the CH bonds are polarised C^{δ-}-H^{δ+}, as is indicated from the population analyses

TABLE 5
Population analyses for thiophen, its *S*-oxide, and SS-dioxide

(a) Total Thiophen (1)							
	S	C(2),C(5)	C(3),C(4)	H(2),H(5)	H(3),H(4)	O	
<i>sp</i>	15.8563	6.2393	6.1654	0.8266	0.8404		
<i>spd</i> + 3 <i>s</i> ¹	15.9725	6.1653	6.1657	0.8368	0.8451		
<i>S</i> -Oxide (2) (non-planar; h 0.2; θ 135°)							
<i>sp</i>	15.2482	6.2436	6.1500	0.8120	0.8264	8.6877	
<i>spd</i> + 3 <i>s</i> ¹	15.5020	6.1716	6.1487	0.8216	0.8307	8.5526	
<i>SS</i> -Dioxide (3) (OSO angle, 120°)							
<i>spd</i> + 3 <i>s</i> ¹	15.1101	6.1637	6.1261	0.8092	0.8170	8.5288	
(b) Components of population							
	Thiophen			<i>S</i> -Oxide (as above, <i>spd</i> + 3 <i>s</i> ¹)			
	S	C(2),C(5)	C(3),C(4)	O	S	C(2),C(5)	C(3),C(4)
1 <i>s</i> + 2 <i>s</i> + 3 <i>s</i> + 3 <i>s</i> ¹	5.7404	3.0791	3.0536	3.8855	5.5131	3.0852	3.0614
2 <i>p</i> + 3 <i>p</i>	10.0856	3.0862	3.1121	4.6670	9.5168	3.0865	3.0874
3 <i>d</i>	0.1464				0.4721		
<i>SS</i> -Dioxide (as above, <i>spd</i> + 3 <i>s</i> ¹)							
	O		S		C(3),C(4)		
1 <i>s</i> + 2 <i>s</i> + 3 <i>s</i> + 3 <i>s</i> ¹		3.8765	5.2871	3.0822		3.0687	
2 <i>p</i> + 3 <i>p</i>		4.6523	8.9284	3.0815		3.0574	
3 <i>d</i>			0.8946				

S=O systems,³⁸ the latter of which has a pair of bent SO bonds of kinetic energy 2.3140 a.u. (*cf.* 2.2486 a.u. here). There are two lone pairs on oxygen in (2); these are of similar *sp* character and their positions are nearly symmetrical on opposite sides of the SO bent bond plane. Again these pairs can be resolved into a pair along the SO axis and one perpendicular to the SO bent bond plane. The kinetic energy of the oxygen lone pairs is similar to those in water (2.9787 a.u.), S₂O (3.1462 and 3.1925 a.u., non-equivalent),³⁸ and SOCl₂ (2.9430 a.u.).^{39,*}

Although the *SS*-dioxide (3) shows S=O groupings, there are significant differences to the bonding of the sulphoxide. Thus the orbitals lie along the symmetry

* It is worth noting that in SOCl₂ a localised orbital description³⁹ appears to indicate an SO triple bond and single O lone pair; the kinetic energy of the pair of equivalent SO bonds (2.2727 a.u.) is very similar to that in the present work, while that of the unique one (2.4166 a.u.) is rather different. Most properties suggest an SO double bond in SOCl₂.²²

below. This suggests that the latter gives a correct sign for this bond, and that frequent suggestions of a reverse polarisation are incorrect. The CS bonds are virtually non-polar, while the SO bonds are polarised towards oxygen, views again consistent with the population analyses.

The population analyses (Table 5 and 6) give an alternative method for the interpretation of the bond polarity. We give data for thiophen (1) the non-planar *S*-oxide (2), and the *SS*-dioxide (3) with the geometry of (2) and (3) as close to the optimum as possible; in fact for the *S*-oxide (2), the total populations are virtually unchanged between the planar and pyramidal states [(planar: S, 15.5055; O, 8.5109; C(2),C(5), 6.1594; C(3),C(4) 6.1682)]. We have discussed the populations in

³⁸ R. H. Findlay, unpublished observations.

³⁹ M. F. Guest and I. H. Hillier, *Internat. J. Quantum Chem.*, 1972, **6**, 967.

thiophen previously,^{5,40} and here we consider trends in the series (1)—(3). The CH bonds, although containing an internal dipole, are effectively neutral overall, as are the CS bonds; in the latter case the addition of $3s^1_s$ [populations: (2), 0.3607; (3), 0.3492] and $3d_s$ functions

TABLE 6

Population in the π -orbitals of thiophen and the planar S-oxide				
	O	S	C(2),C(5)	C(3),C(4)
Thiophen				
$2b_1$		0.5971	0.3690	0.3324
$3b_1$		1.1395	0.0031	0.4272
$1a_2$		0.0273	0.7144	0.2720
S-Oxide (planar)				
$2b_1$	0.05014	0.9759	0.1716	0.0898
$3b_1$	0.7556	0.0781	0.2115	0.3717
$4b_1$	0.5795	0.7331	0.0091	0.3346
$1a_2$	0.0280	0.0854	0.6737	0.2676

reduces the polarity,^{5,41} and provides a refinement of the wave-function in the neighbourhood of sulphur. The oxygen atoms are heavily negatively charged, even with the largest ($spd + 3s^1$) basis set, and values near $S^{+0.5}$ — $O^{-0.5}$ are clear in each case. Overall the $3d$ functions play an increasing role in the series (1)—(3) as evidenced by their total populations.

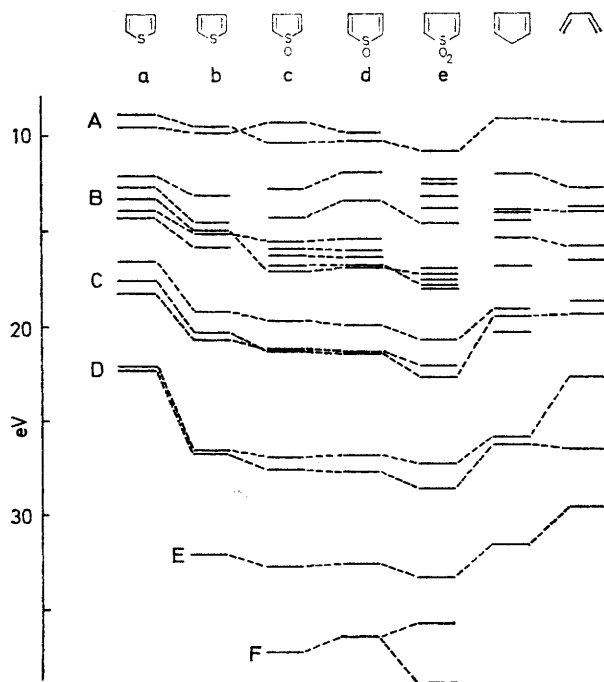
Molecular Orbital Energy Levels.—In this section we carry out a partial correlation of the orbitals of (1)—(5). The experimental photoelectron spectrum of thiophen (1)⁴¹ shows four main regions (A—D) of ionisation potential (Figure), and 12 IPs have been identified. These may be directly correlated^{40,42} with the experimental spectrum in preference to earlier semi-empirical results.⁴¹

Although the second region (B) is more diffuse, again a direct correlation between the orbital energies and the photoelectron spectra is possible for cyclopentadiene (4).⁴³ For the S-oxide (3) and SS-dioxide (4) additional regions E and F occur, with only the former in thiophen; as can be seen the planar—pyramidal change only shifts the energy levels by small amounts (Figure; C,D). The structural change (1) \rightarrow (3) leads to break-up of region B, but the other regions remain largely unchanged along the series (1)—(4); thus we anticipate that photoelectron spectra for (2) and (3) will reproduce the groups shown, but owing to the large number of ionisations within the groups B, the internal order in a group cannot be regarded as unambiguous.

We have noted previously³⁻⁵ that many of the changes in relative positions of particular molecular symmetry orbitals in a series of compounds can be rationalised in terms of the free atom energy levels. Relevant ones for the present series, at the Hartree-Fock limit,²² are C; 2s, 19.20; $2p$, 11.79; O, 2s, 33.86; $2p$, 17.20; S; 3s, 23.94; $3p$, 11.90; H; 1s, 13.61 eV. The high binding energy of $2s_0$ relative to the other orbital energies is responsible

* In (6)—(8), the signs (\pm) indicate the symmetry and nodal positions of the wave function. These designations are equally applicable to s - or p_{π} -functions.

for the high degree of localisation of the region F orbitals. In contrast the relatively close $3s_s$ and $2s_0$ energies leads to considerable mixing and the formation of region E molecular orbitals [$2s$ levels as in (6)], with a trend to higher binding energy as the electronegativity of the group X ($CH_2 \sim S < SO < SO_2$) increases; a similar trend with the antisymmetric level [b_2 , (7)] of the D region occurs, and this arises from the varying levels of the tangential $2p_x$ atomic orbital (*cf.* ref. 3); both these last two effects are observed in the azines.³ In general the a_1 — b_2 separation [(7), (8)]* in the C_{2v} molecules (1)—(4) is not high, and is reminiscent of the corresponding degenerate level (e^1) in the cyclopentadienyl



Experimental photoelectron spectra of compounds (1)—(5)

anion. In contrast the corresponding levels in *cis*-buta-1,3-diene ($3b_2$ and $4a_1$) are separated by 4.0 eV; this difference arises from the ability of the cyclic system to stabilise the bonding between the two ends of the four carbon skeleton [as in (8)], and no such stabilisation can occur with butadiene. Two remaining $2s_0$ — $2s_x$ — $3s_x$ levels occur, but with extensive CH and CS bonding character (region C); again in this region the binding energy shows a progressive increase as the electronegativity of the heteroatom X increases, through contributions from either the s -(a_1) or tangential p -orbitals (b_2). Above this region, very few orbitals can be correlated along the series (1)—(5), but some of the b orbitals are largely unchanged across parts

⁴⁰ M. H. Palmer and R. H. Findlay, *J.C.S. Perkin II*, 1975, 974.

⁴¹ P. J. Derrick, L. Asbrink, O. Edqvist, B.-O. Jonsson, and E. Lindholm, *Internat. J. Mass Spectrometry Ion Phys.*, 1971, **6**, 177.

⁴² U. Gelius, B. Roos, and P. Siegbahn, *Theor. Chim. Acta*, 1972, **27**, 171.

⁴³ S. Craddock, R. H. Findlay, and M. H. Palmer, *J.C.S. Dalton*, 1974, 1650.

of the series, owing to being either nodal at X, or containing only transverse CX binding character (*cf.* ref. 4).*

Aromaticity and Diels–Alder Reactivity Considerations.—We now consider reasons for the non-planarity of the thiophen ring in the S-oxide (2), noting that whilst sulphoxides (and also phosphines) are pyramidal,^{12,32,33} this could have been achieved in the sulphoxide (or phosphole) merely by out-of-plane movement of the oxygen (or hydrogen atom). Addition of an oxygen atom to the thiophen ring yielding the planar sulphoxide, if a triplet state is to be avoided, must be by the form $O(1s^2 2s^2 2p_\pi^2 2p_\sigma^2)$ thus leading to an 8π valency shell system. The high binding energy of $2p_{O^\pi}$ leads to the primary interaction with $2b_1$ (6), where \dagger represents the phase of the π -orbitals, rather than $3b_1$ (8). The former is a heavily delocalised orbital owing to the energy proximity of $2p_C$ and $3p_S$, which is thus lowered sharply in energy [yielding $2b_1$ in (2)] but more localised in character. The orbital $3b_1$ in (2) is the corresponding SO antibonding mixture of $2b_1$ in (1) and oxygen, and this as well as $4b_1$ in (2) [which is analogous to $3b_1$ in (1)] both remove significant amounts of π -electron density from the ring. The orbital $1a_2$ in both (1) and (2) is largely unaffected by the addition of oxygen to (1), the small shift arising from the increased $3d_S$ component in (2) when compared with (1). Thus overall the oxygen atom is strongly electron withdrawing in the π -system (Table 6), leading to a loss of aromatic character in the planar system. We have previously noted that aromatic character runs parallel to the degree of sextet character in 6π valency shell systems; comparison of planar (2) with (1) (Table 7) shows how the π -electrons are drawn

TABLE 7

Average positions of the π -electrons from $C_\beta C_\beta$ bond (Å)				
	$2b_1$	$3b$	$4b_1$	$1a_2$
Thiophen (1)	1.169	1.395		0.941
S-Oxide (2)	2.425	1.871	1.969	0.969

towards oxygen, with a consequent decline in delocalised character. In the non-planar sulphoxide with only

* Opposite assignments to the IPs at 10.26 and 12.58 eV have recently been given for dimethyl sulphoxide.^{16,17} If the present work can be extended to the simple aliphatic system then the present order tends to support CNDO/2 calculations.¹⁷

† The mass spectrum of the tricarbonyl iron complex has loss of SO_2 as the first peak involving the heterocyclic ring.⁴⁴

oxygen out of plane no clear separation is possible for the σ - and π -systems, but the insignificant changes in population at the various centres during the binding process noted above, show that the π -electron sextet is unlikely to be retained in this form. Thus the movement to the pyramidal form with both S and O out of plane (as in phospholes) occurs, with $3s$ - $3p$ mixing and modification of the σ -levels, and increased isolation of the two functional groups.

Finally we suggest that in conjugated compounds the tendency towards Diels–Alder addition or self-condensation can be correlated with the ratio (R) of the overlap populations in the formal double and single bonds; this is a non-empirical procedure closely aligned to the bond order description of Hückel theory. In Table 8, using

TABLE 8

	Diels–Alder reactivity indices		
	Overlap populations ^a		
	C(2)–C(3)	C(3)–C(4)	Ratio R
Benzene	0.5206	0.5206	1.000
Phosphorin	0.5197	0.5164	1.006
Pyrrole	0.5777	0.4916	1.175
Thiophen	0.5950	0.4774	1.246
Furan	0.6837	0.5329	1.283
Phosphole (planar)	0.6058	0.4684	1.293 ^b
Thiophen S-oxide	0.5938	0.4558	1.302 ^{b,c}
Phosphole (pyramidal)	0.6124	0.4459	1.374 ^b
Thiophen SS-dioxide	0.6091	0.4213	1.445
Cyclopentadiene	0.6215	0.4288	1.449
cis-Butadiene	0.6076	0.4034	1.506

^a All calculated with the same C, H, N, O, S, P basis as appropriate. ^b $sp^d + 3s^1$ basis; similar figures for other bases. ^c Final optimum geometry (see text).

benzene and cyclopentadiene as standards for aromatic and diene character respectively, we note that the higher dienic character of the S-oxide (2) and SS-dioxide (3) † relative to thiophen (1). This is consistent with the tendency of (2) and (3) towards self-condensation. The series (Table 8) runs from stable monomers (benzene, furan) to unstable monomers (thiophen S-oxide, cyclopentadiene); the position of phosphole suggests that it is likely to be isolated as a dimer.

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⁴⁴ Y. L. Chow, J. Fossey, and R. A. Perry, *J.C.S. Chem. Comm.*, 1972, 501.