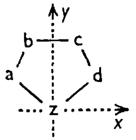
444. *Calculation of Some π-Electron States in Furan, Thiophen, and the Parent Hydrocarbon Compound using Valence-bond Approximation.*

By A. Mangini and C. Zauli.

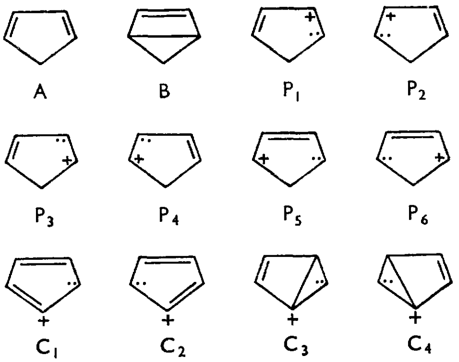
The first few singlet states in furan, thiophen, and cyclopentadiene have been theoretically investigated by the modified valence-bond technique described in the preceding paper.

Values of 7·4, 6·2, and 4·7 ev, respectively, have been found for the first allowed transition ($A_1 \longrightarrow B_1$), in reasonable agreement with experimental data; other molecular parameters, such as resonance energy and charge distribution, have been computed. The results have been discussed in relation to the near-ultraviolet spectra and chemical reactivities: as expected, the diene system in thiophen has been found to be much more perturbed than that in furan.

In a previous paper[1] the authors discussed from a theoretical point of view the modification of the near-ultraviolet spectrum of benzene by heteroatoms with a π-orbital doubly filled, *e.g.*, by oxygen and sulphur in monosubstituted benzene derivatives. The present work is a valence-bond study of five-membered cyclic aromatic compounds such as thiophen and furan and is designed to afford information on the rôle played by sulphur and oxygen in the nucleus.[2]



(X)



Structures of set (I).

For comparison, a *cis*-butadiene-like molecular arrangement, representing the parent hydrocarbon compound cyclopentadiene, has also been studied. Since the number of electrons involved is too large for a comprehensive theoretical treatment, the π-approximation has been used. This consists in studying a π-electron problem in the field of ionised atoms which results from extracting the π-electrons; no account is thus taken of hydrogen atoms and underlying σ-bonding. It is emphasized that this approximation disregards the difference of σ–π interaction in the various π-states, and affects the calculation by an unknown amount.

The modified valence-bond procedure proposed in the preceding paper[3] has been applied. The parent hydrocarbon is treated as cyclopentadiene, the influence of the $-CH_2-$ group being totally disregarded, thus excluding *a priori* hyperconjugative effects,[4]

---

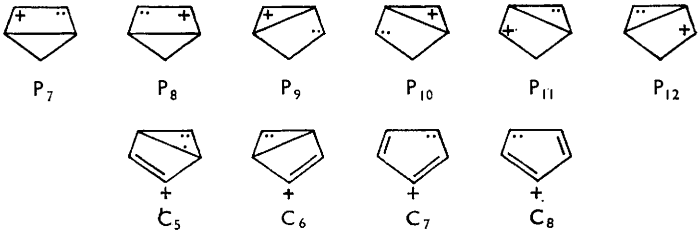
[1] Mangini and Zauli, *J.*, 1956, 4960.

[2] Cf. Mangini, *J. Chim. Phys.*, 1959, **56**, 240.

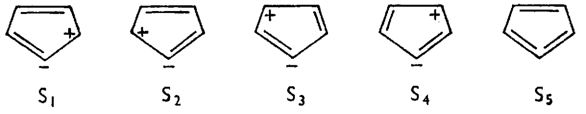
[3] Zauli, preceding paper.

[4] Mulliken, *J. Chem. Phys.*, 1939, **7**, 339.

in accord with the arguments of Price and Walsh.[5] All the molecules concerned then present the same molecular arrangement (X) in which a, b, c, d, are four $2p_\pi$atomic orbitals of carbon atoms and z is an oxygen $2p_\pi$, sulphur $3p_\pi$ or a $-CH_2-$ group. All atomic orbitals are of Slater's type without radial nodes. Therefore, in the framework of a π-approximation, the calculations will deal with a four-π-electron problem in the field of four singly ionised carbon atoms (cyclopentadiene), and two six-π-electron problems in the field of four singly ionised carbon atoms and of a doubly ionised oxygen or sulphur atom (furan and thiophen, respectively). Only singlet states will be considered, the structures chosen to represent the resonating systems[6] being set (1). The C_n structures occur in furan and thiophen, but not in cyclopentadiene. Structures other than those of set (1) should also be considered, namely, set (2), and others with two or three centres of negative charge; however, their inclusion would probably have little effect on the energies of ground and first excited states of the three molecules [although the coefficients of set (1) structures in the respective eigen-functions may be modified] because a structure with a bond between non-neighbouring atoms has been calculated to be less stable by ~2 ev than one with a bond between neighbouring atoms, and the energy difference between a covalent structure and a polar one is at least 3·5—4 and 6 ev if the formal charges are on neighbouring or non-neighbouring atoms respectively. Larger energy differences are to be expected in the case of doubly or higher excited structures.



Structures of set (2).



Structures of set (3).

Structures with a negatively charged sulphur such as those of set (3) have been excluded for thiophen since they involve the participation of $3d$-atomic orbitals. Shomaker and Pauling,[7] from dipole-moment data and bond lengths, inferred a 10% contribution by S_n structures to the ground state, but apart from the obvious difficulties in dealing with a larger number of atomic orbitals, we do not hold expansion of the valency shell of sulphur in aromatic compounds to have been proved, except for sulphoxides and sulphones;[8] indeed, from a spectroscopic point of view, as one of us[2] has shown, no evidence exists for aromatic sulphides. Longuet-Higgins[9] showed theoretically that an analogy might be drawn between $-CH=CH-$ and $-\dot{S}-$, using $3p$–$3d$ hybrids of the latter, and other authors[10,11]

---

[5] Price and Walsh, *Proc. Roy. Soc.*, 1941, *A*, **179**, 201.

[6] See Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953, p. 174.

[7] Shomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1779.

[8] Koch and Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7.

[9] Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173.

[10] Metzger and Ruffler, *J. Chem. Phys.*, 1954, **51**, 52.

[11] De Heer, *J. Amer. Chem. Soc.*, 1954, **76**, 4802.

have agreed. However, it can be shown * that by using Longuet-Higgins's assumptions, for thiophen and for all sulphides with a CSC valency angle of ~90°, the three hybrids built with $3p_z$, $3d_{xz}$, $3d_{yz}$ sulphur atomic orbitals have mainly *d*-character, and so have an impossibly large energy.

By using the symmetry properties of the C_{2v} group from structures (1) the following total molecular functions of A_1 and B_1 symmetry have been built:

$$\Psi_{A1} = \gamma_1\mathrm{A} + \gamma_2\mathrm{B} + \gamma_3[\mathrm{C}_1 + \mathrm{C}_2] + \gamma_4[\mathrm{C}_3 + \mathrm{C}_4] + \gamma_5[\mathrm{P}_1 + \mathrm{P}_2] + \gamma_6[\mathrm{P}_3 + \mathrm{P}_4] + \gamma_7[\mathrm{P}_5 + \mathrm{P}_6] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\Psi_{B1} = \delta_1[\mathrm{C}_1 - \mathrm{C}_2] + \delta_2[\mathrm{C}_3 - \mathrm{C}_4] + \delta_3[\mathrm{P}_1 - \mathrm{P}_2] + \delta_4[\mathrm{P}_2 - \mathrm{P}_3] + \delta_5[\mathrm{P}_5 - \mathrm{P}_6] \quad . \quad (2)$$

In the case of cyclopentadiene γ_3, γ_4, δ_1, δ_2 are zero.

As the results for cyclopentadiene show, γ_7 is very small and consequently, in order to reduce further the secular equations of furan and thiophen, γ_7 has been assumed to be zero. At this stage the procedure previously outlined[3] was applied to compute matrix elements, and the secular equations were solved. The exponential factors in atomic orbitals were obtained from Kohlrausch's table;[12] for cyclopentadiene[13] the calculation has been repeated with Slater's value for the carbon atomic orbitals (see Appendix).

Table 1 shows energy values in Rydberg units for the first few states. Here the asterisk indicates the first excited state of A_1 symmetry and Q^c, Q^f, Q^t are the coulombic integrals relative to a covalent structure of cyclopentadiene, furan, and thiophen respectively.

TABLE 1.

	Cyclopentadiene ‡			
State	*a*	*b*	Furan	Thiophen
A_1	$Q^c - 0{\cdot}142$	$Q^c - 0{\cdot}514$	$Q^f - 0{\cdot}034$	$Q^t - 0{\cdot}066$
A_1 *	$Q^c + 0{\cdot}250$	—	$Q^f + 0{\cdot}498$	$Q^t + 0{\cdot}366$
B_1	$Q^c + 0{\cdot}203$	$Q^c + 0{\cdot}505$	$Q^f + 0{\cdot}509$	$Q^t + 0{\cdot}387$

(*a*) ‡ Kohlrausch's and (*b*) Slater's value employed for orbital exponents.

The γ's and δ's corresponding to the first state of each symmetry are listed in Table 2.

TABLE 2.

	Cyclopentadiene					Cyclopentadiene			
γ	*a*	*b*	Furan	Thiophen	δ	*a*	*b*	Furan	Thiophen
γ_1	0·47	0·53	0·16	0·04	δ_1	—	—	0·40	1·04
γ_2	−0·17	−0·11	−0·13	−0·18	δ_2	—	—	0·06	0·77
γ_3	—	—	0·30	0·46	δ_3	0·35	0·48	0·24	0·09
γ_4	—	—	−0·16	−0·19	δ_4	−0·52	−0·57	−0·43	−0·29
γ_5	0·17	0·32	0·22	0·12	δ_5	0·46	0·54	0·43	0·13
γ_6	0·28	0·33	0·32	0·33					
γ_7	0·14	0·08	—	—					

From Table 1 the first transition energies can be obtained: the experimental and calculated values (in ev) are compared in Table 3. The agreement is reasonable and the errors are of the order of magnitude expected from an approximate treatment.

* Referring to Longuet-Higgins's paper, the three hybrids, Φ_f Φ_g, Φ_h, are:

$$\Phi_{,g} = \frac{S_{ac}S_{ae}\Phi_c + S_{ad}S_{ac}\Phi_d \pm (S_{ac}^2 + S_{ad}^2)\Phi_e}{\{(S_{ac}^2 + S_{ad}^2)(S_{ac}^2 + S_{ad}^2 + S_{ae}^2)\}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

$$\Phi_h = \frac{S_{ad}\Phi_e - S_{ac}\Phi_d}{(S_{ac}^2 + S_{ad}^2)^{\frac{1}{2}}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (b)$$

If it is assumed that S_{ad}/S_{ac} is small, as Longuet-Higgins does in his paper (p. 176), and CSC angle is ~90°, then S_{ae}/S_{ac} is also small and Φ_f, Φ_g, Φ_h all reduce to a 3*d*-orbital, as may be seen from (*a*) and (*b*); more exactly:

$$\left.\begin{array}{r} \Phi_f \text{ and } \Phi_g \longrightarrow \Phi_e \\ \Phi_h \longrightarrow \Phi_d \end{array}\right\} \text{for } \frac{S_{ad}}{S_{ac}} \text{ and } \frac{S_{ae}}{S_{ac}} \text{ small.}$$

[12] Kohlrausch, *Acta Phys. Austriaca*, 1950, **3**, 452.

[13] See Berry, *J. Chem. Phys.*, 1957, **26**, 1660.

TABLE 3.

Cyclopentadiene			Furan		Thiophen		Type of transition
calc.							
a	*b*	exp.	calc.	exp.	calc.	exp.	
5·3	—	—	7·2	—	5·9	—	$A_1 \longrightarrow A_1^*$ (*y*)
4·7	13·9	4·8 [p]	7·4	6·1 [5,q]	6·2	5·4 [5]	$A_1 \longrightarrow B_1$ (*x*)

[p] Landolt–Börnstein, " Tabellen," Vol. I, Part 3, p. 705. [q] Pickett, Hoeflich, and Tien Chuan Liu, *J. Amer. Chem. Soc.*, 1951, **73**, 4865.

Interesting features from this Table are the following: (*a*) The direction of the shift when passing from cyclopentadiene to thiophen and furan is correctly represented. Since no hyperconjugative effects and no 3*d* atomic orbitals have been taken into consideration the results suggest that the main cause of the observed shift is not to be found in these effects but is inherent in the π-systems. On the other hand, it is impossible to correlate it with a simple parameter: all that can be said is that the observed blue shift is mainly due to a raising of the first excited state, following the order of ionisation potentials of sulphur and oxygen. (*b*) The $A_1 \longrightarrow A_1^*$ transitions occur very near to the strongly allowed $A_1 \longrightarrow B_1$ transitions.

An interpretation of Table 2 in terms of weights of structures is not possible because terms such as $\int \mathrm{MHN}\, d\tau$, where M and N are structures, participate in the mesomeric system with weight $2\gamma_{\mathrm{M}}\gamma_{\mathrm{N}}$. However, with the rough assumption that

$$\int \mathrm{MHN}\, d\tau = S_{\mathrm{MN}}/2\left[\int \mathrm{MHM}\, d\tau + \int \mathrm{NHN}\, d\tau\right] \quad . \quad . \quad . \quad . \quad (3)$$

the weights in Table 4, indicated conventionally by γ_n^2 or δ_n^2, relative to structures of set (1) in the first state of each symmetry have been obtained. Interpretation of this Table is not yet straightforward from a chemical point of view: for example, $[\mathrm{P}_5 + \mathrm{P}_6]$ in expression (1) (which may be considered as one structure since it is normalized), although composed of formally polar structures, does not describe charge migrations and consequently may be regarded as a covalent structure in which both electrons of the *a–d* bond are to be found with a 25% probability localized either on atom *a* or on atom *b*. It follows that the chemical structure with an α–α and a β–β bond is represented here by the sum of B and $[\mathrm{P}_5 + \mathrm{P}_6]$ {and of course $[\mathrm{P}_7 + \mathrm{P}_8]$ if it had been considered in expression (1)}.

TABLE 4.

	Cyclopentadiene					Cyclopentadiene			
γ_n^2	*a*	*b*	Furan	Thiophen	δ_n^2	*a*	*b*	Furan	Thiophen
γ_1^2	0·45	0·48	0·14	0·03	δ_1^2	—	—	0·24	0·70
γ_2^2	0·13	0·07	0·10	0·13	δ_2^2	—	—	−0·02 *	0·05
γ_3^2	—	—	0·22	0·38	δ_3^2	0·24	0·28	0·14	0·03
γ_4^2	—	—	0·12	0·15	δ_4^2	0·40	0·37	0·30	0·14
γ_5^2	0·14	0·21	0·16	0·07	δ_5^2	0·36	0·35	0·34	0·08
γ_6^2	0·24	0·23	0·25	0·24					
γ_7^2	0·04	0·01	—	—					

* The negative sign is probably a result of approximation (3). The exponential factor is much less critical in the determination of weights than of energies, as columns *a* and *b* show.

Analogously, the chemical structure with two α–β bonds is represented by the sum of A, $[\mathrm{P}_1 + \mathrm{P}_3]$ and $[\mathrm{P}_2 + \mathrm{P}_4]$: since $[\mathrm{P}_1 + \mathrm{P}_2]$ and $[\mathrm{P}_3 + \mathrm{P}_4]$ are found in expression (1) it is necessary to rewrite it in a more convenient form. With care in handling the normalization coefficients, eqn. (1) for the ground state of the π-electron systems considered may be written as follows:

Cyclopentadiene:

$$\Psi_{A_1} = 0{\cdot}473\mathrm{A} + 0{\cdot}162[\mathrm{P}_1 + \mathrm{P}_3] + 0{\cdot}162[\mathrm{P}_2 + \mathrm{P}_4] - 0{\cdot}170\mathrm{B} + 0{\cdot}125[\mathrm{P}_5 + \mathrm{P}_6] + \\ 0{\cdot}122[\mathrm{P}_3 + \mathrm{P}_4] \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Furan:

$$\Psi_{A_1} = 0{\cdot}164\mathrm{A} + 0{\cdot}214[\mathrm{P}_1 + \mathrm{P}_3] + 0{\cdot}214[\mathrm{P}_2 + \mathrm{P}_4] - 0{\cdot}133\mathrm{B} + 0{\cdot}091[\mathrm{P}_3 + \mathrm{P}_4] + 0{\cdot}305[\mathrm{C}_1 + \mathrm{C}_2] - 0{\cdot}164[\mathrm{C}_2 + \mathrm{C}_4] \quad . \quad (5)$$

Thiophen:

$$\Psi_{A_1} = 0{\cdot}035\mathrm{A} + 0{\cdot}114[\mathrm{P}_1 + \mathrm{P}_3] + 0{\cdot}114[\mathrm{P}_2 + \mathrm{P}_4] - 0{\cdot}175\mathrm{B} + 0{\cdot}208[\mathrm{P}_3 + \mathrm{P}_4] + 0{\cdot}458[\mathrm{C}_1 + \mathrm{C}_2] - 0{\cdot}189[\mathrm{C}_3 + \mathrm{C}_4] \quad . \quad (6)$$

In eqns. 4—6 the first three terms represent a situation in which bonds exist between a and b, and between c and d; the fourth (and in cyclopentadiene the fifth) term is one in which a,d and b,c are bound and no charge migration is present; $[P_1 + P_3]$, $[P_2 + P_4]$, $[P_5 + P_6]$ represent electronic localisation on the various carbon atoms. The last terms are associated with a charge migration and can be conveniently grouped in two classes: (i) terms that describe electron migrations formally derived from a covalent structure, here generically called polar (or ionic) structures; and (ii) terms not derivable from a covalent structure, here called conjugate structures.

By using eqn. (3) again, the weights given in Table 5 were obtained for $[P_1 + P_3]$, $[P_2 + P_4]$, and $[P_3 + P_4]$, here conventionally indicated by $\gamma_5^{2\prime}$ and $\gamma_6^{2\prime}$ respectively (the other γ^2's remaining unchanged). These yield weights of 73, 48, and 19 relative to the chemical structure with two α–β bonds in cyclopentadiene, furan, and thiophen respectively.

TABLE 5.

	Cyclopentadiene	Furan	Thiophen
$\gamma_5^{2\prime}$	0·14	0·17	0·08
$\gamma_6^{2\prime}$	0·10	0·07	0·15

An attempt has also been made to calculate the resonance energy in furan and thiophen by supposing it to be the difference between the ground-state energy and that of the covalent structure with two α–β bonds: by using eqns. (5) and (6) the normalized functions Φ_F and Φ_T corresponding to such structures are found to be:

$$\Phi_F = 0{\cdot}306\mathrm{A} + 0{\cdot}399[\mathrm{P}_1 + \mathrm{P}_3] + 0{\cdot}399[\mathrm{P}_2 + \mathrm{P}_4] \quad . \quad . \quad . \quad . \quad (7)$$

$$\Phi_T = 0{\cdot}135\mathrm{A} + 0{\cdot}435[\mathrm{P}_1 + \mathrm{P}_3] + 0{\cdot}435[\mathrm{P}_2 + \mathrm{P}_4] \quad . \quad . \quad . \quad . \quad (8)$$

Accordingly the calculated resonance energies are for furan 37 and for thiophen 56 kcal./mole. Since these have been calculated without a nuclear repulsion correction,[14] they compare favourably with the experimental values[15] of 16 and 29 kcal./mole respectively.

From Tables 4 and 5 the charge distribution in the ground state of cyclopentadiene, furan, and thiophen can be approximately derived; the results (d) in Table 6 are shown with those (e) obtained by Daudel *et al.*[16] for furan and thiophen and by Kikuchi[17] for thiophen (f) using the molecular-orbital method.

TABLE 6.

	Cyclopentadiene	Furan		Thiophen		
Atom	d	d	e	d	e	f
a	+0·050	−0·140	−0·030	−0·190	−0·090	−0·025
b	−0·050	−0·035	−0·015	−0·075	−0·050	−0·017
z	—	+0·350	+0·080	+0·530	+0·280	+0·088

---

[14] Coulson, " Valence," Clarendon Press, Oxford, 1952, p. 236.

[15] Klages, *Chem. Ber.*, 1949, **82**, 358.

[16] Daudel, Buu-Hoï, and Martin, *Bull. Soc. chim. France*, 1948, **15**, 1202.

[17] Kikuchi, *Sci. Rep. Tohôku Univ.*, **1957**, **41**, 35.

In Table 7 are collected the values for the probability of finding a negative or a positive charge on a given atom. Since the probability of finding a negative charge may be interpreted as the chance of having two electrons on the atom it is clear that twice this figure gives the fraction of electrons that do not participate in bonds with neighbour atoms, *i.e.*, the free negative charge. This holds for carbon atoms; for heteroatoms the free charges are O = 1·30*e*, S = 0·94*e*.

TABLE 7. *Probability of finding a positive or negative charge on different atoms.*

	Negative charge			Positive charge		
Atom	Cyclopentadiene	Furan	Thiophen	Cyclopentadiene	Furan	Thiophen
a	0·045	0·217	0·285	0·095	0·077	0·095
b	0·085	0·077	0·095	0·035	0·042	0·020
z	—	—	—	—	0·350	0·530

Bak [18] deduced from microwave data the distribution of free charge in furan, which is shown in Table 8 with our results. However these figures are not strictly comparable since the present authors have included structures such as [$C_3 + C_4$] which allow electrons inside the ring, and Bak considered only peripheral bonds. For thiophen Bak *et al.*[19] inferred a withdrawal of 0·60*e* from the sulphur atom, a value very close to 0·53*e* found in the present work.

TABLE 8.

Atom	Bak's results	Present work
a	0·25	0·44
b	0·10	0·15
z	1·41	1·30

Bearing in mind the data collected in Tables 4—8 we may summarise the situation which arises from the present work as follows:

Ground state: The weight of covalent structures follows the series cyclopentadiene (90%) > furan (58%) > thiophen (32%), and that of conjugated structures thiophen (53%) > furan (35%). This clearly indicates the perturbation of the diene system to be larger in thiophen than in furan, in agreement with the chemical observation that furan may behave as a diene and thiophen does not. The calculated charge distributions show that the 2-position is the more negative in both heterocyclic compounds, again in agreement with the chemical evidence on electrophilic substitutions: acylation [20] and chlorination [21] lead to more than 99% of the 2-thiophen derivative, and in furan the 2-position is always preferred.[22]

Both the 2- and the 3-position in thiophen show a negative charge larger than that in the corresponding position in furan: this does not necessarily mean that thiophen is more reactive in substitutions because a main factor here is represented by the energies of the transition complex; experimentally, furan is found to undergo substitutions more easily than thiophen in the 2-position, less easily in the 3-position.

Higher free charge on oxygen may explain the easy protonisation in furan that ultimately leads to the ring cleavage.

No explanation is offered here for the fact that furan undergoes the diene reaction (Diels–Alder) and thiophen does not. If the energy of the transition complex is approximated to the energy of the structure with a β–β and an α–α bond (since the latter is likely to contribute very little to the total energy) we obtain the following tentative transition energies: cyclopentadiene 2·4, furan 4·7, thiophen 4·6 ev.

[18] Bak, *Acta Chem. Scand.*, 1955, **9**, 1355.

[19] Bak, Christensen, Rastrup-Andersen, and Tannenbau, *J. Chem. Phys.*, 1956, **25**, 892.

[20] Hartough *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 1012, 1014, 3093, 3096, 3098; 1948, **70**, 867.

[21] Conradt and Hartough, *J. Amer. Chem. Soc.*, 1948, **70**, 1158, 2564.

[22] Dunlop and Peters, " The Furans," Reinhold Publ. Inc., New York, 1953, p. 6.

Evidently if these values (not corrected for the charge transfer probably present in the transition state [23]) explain the low energy barrier existing for cyclopentadiene, they do not distinguish between furan and thiophen.

It must be stressed again, however, that the static properties here described are not sufficient to interpret the whole process, and the dynamic behaviour of the system of reacting molecules is probably more important.

When we come to consider the first excited state of B_1-symmetry, the weight of conjugated structures increases from zero in cyclopentadiene to 1/4 in furan and 3/4 in thiophen. This, together with the results for the ground state, may well be related to the large amount of dienic character [5,24] presented by the first band of furan and absent in the corresponding band of thiophen.

At this stage the behaviour of sulphur and oxygen when in side-chain or in the aromatic nucleus may be compared. In monosubstituted benzene derivatives the ground state is less modified from in the corresponding heterocyclic compounds: moreover, the conjugative power of sulphur and oxygen is reversed.[25,26] The excited B_{2u} state of benzene is modified by sulphur but still retains its benzenoid character; in thiophen the B_1 state is quite different from that of cyclopentadiene, being composed almost entirely of conjugated structures. The oxygen derivatives on the contrary are more analogous to those of benzene.

It must be emphasised that the foregoing discussion is merely qualitative. Rather a large number of approximations, unavoidable at this stage, has been employed. Some others, relative to the computation of atomic integrals, are reported in the Appendix.

APPENDIX

The interatomic distances (in Å) of the models adopted in the present calculations are summarized in Table 9. Those relative to thiophen and cyclopentadiene are based essentially upon the furan model recently proposed.[27]

TABLE 9. *Interatomic distances.*

Atoms	Cyclopentadiene	Furan	Thiophen *	Atoms	Cyclopentadiene	Furan	Thiophen *
ab	2·564	2·564	2·564	bc	2·695	2·695	2·695
ac	4·393	4·216	4·393	az	—	2·596	3·287
ad	4·714	4·157	4·714	bz	—	4·233	4·819

* Recent microwave data for thiophen are given by Bak *et al.*[19]

The exponential factors in the atomic orbitals were $K_C = 1{\cdot}043$, $K_O = 1{\cdot}450$, $K_S = 1{\cdot}282$, $\bar{K}_C = 1{\cdot}834$, $\bar{K}_O = 2{\cdot}461$, $\bar{K}_S = 2{\cdot}143$. The bar indicates K-values for positive ions. These have been obtained from Kohlrausch's table; [12] those of oxygen and sulphur were slightly corrected for the polarisation of σ-bonds in furan and thiophen.

Sklar and Liddane's method [28] has been employed to evaluate integrals $(\phi_i V_k \phi_j)$. Atomic integrals containing carbon or oxygen atomic orbitals have been computed exactly.[29] Those containing sulphur $3p_z$ have been computed partly by a method outlined in a previous paper,[1] and the part including nuclear potential by replacement of the sulphur atomic orbital by a $2p_z$ atomic orbital of the same mean radius. Exponential factors for the latter were $K_S = 0{\cdot}911$, $\bar{K}_S = 1{\cdot}466$.

---

[23] Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 3058; Woodward and Baer, *J. Amer. Chem. Soc.*, 1944, **66**, 645.

[24] Pickett-Hoeflich and Tien Chuan Liu, *J. Amer. Chem. Soc.*, 1951, **10**, 4865.

[25] Mangini and Passerini, *Gazzetta*, 1954, **84**, 606.

[26] Lumbroso and Passerini, *Bull. Soc. chim. France*, 1957, 311.

[27] Bak, Hansen, and Rastrup-Andersen, *Discuss. Faraday Soc.*, 1955, **19**, 30.

[28] Sklar and Liddane, *J. Chem. Phys.*, 1939, **7**, 374; cf. Scrocco and Salvetti, *Ricerca Sci.*, 1953, **23**, 1410.

[29] See Barnett and Coulson, *Phil. Trans.*, 1951, **243**, 221; Roothan, *J. Chem. Phys.*, 1951, **19**, 1445; Scrocco and Salvetti, *Ricerca Sci.*, 1952, **22**, 1776.

The monocentric integral has been computed exactly.[30]

A small correction of 0·05 Rydberg unit has been applied to the carbon monocentric integral * in order to satisfy the relation:

$$I_C + (\phi_C\phi_C/\phi_C\phi_C) = E_C \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

where I_C and E_C are the ionisation potential and the electroaffinity respectively of the carbon atom; such a correction may be interpreted as due to electronic correlation in the negative carbon ion. If the exponential factor derived from Slater's rule had been employed, the correction would have been 0·43 unit,[31] as Pariser and Parr [32] used in their semiempirical theory. In the present cyclopentadiene calculations with Slater's exponential factors eqn. (9) was not used since a correlation as large as that mentioned implies that the atomic integrals with two or more centres should also be corrected.[31,33]

In calculating $\bar{T}_{kl}$ functions [3] the following approximation was employed:

$$(\phi_k/-\Delta + V_l/\phi_l) = S_{kl}/2(I_k + I_l) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

where I_k and I_l are the ionisation potentials of atom k and l respectively. Since it has been shown [34] that eqn. (10) is a rather poor relationship a reasonable correction amounting to $-(1/2S_{kl})\phi_l\bar{V}_l\phi_k$, where $\bar{V}_l$ is the potential of the neutral atom l, has been applied to $\bar{T}_{kl}$.

In Table 10 are collected overlap integrals [35] and $\bar{T}_{kl}$ functions for each couple of atomic orbitals.

TABLE 10. *Overlap integrals and $\bar{T}_{kl}$ functions.*

	Cyclopentadiene		Furan		Thiophen	
Couple	$\bar{T}_{kl}$	S_{kl}	$\bar{T}_{kl}$	S_{kl}	$\bar{T}_{kl}$	S_{kl}
ab	−0·207	0·539	−0·207	0·539	−0·207	0·539
ac	−0·172	0·214	−0·179	0·232	−0·172	0·214
ad	−0·158	0·172	−0·182	0·239	−0·158	0·172
bc	−0·215	0·509	−0·215	0·509	−0·215	0·509
az	—	—	−0·531	0·415	−0·310	0·419
bz	—	—	−0·286	0·150	−0·362	0·212

The authors are grateful to Professor C. A. Coulson, F.R.S., for many invaluable suggestions and criticisms. The work was supported in part by the U.S. Army grant.

ISTITUTO DI CHIMICA INDUSTRIALE,
BOLOGNA-UNIVERSITÀ, ITALY.

[*Received, July 20th,* 1959.]

---

* The value of $(\psi_c\psi_c/\psi_c\psi_c)$ here employed is thus 0·7596 Rydberg unit.

[30] Zauli, *Progr. Report Math. Inst.*, Oxford, 1956—7, p. 18.

[31] Kołos, *Acta Phys. Polon.*, 1957, **16**, 229.

[32] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 446, 767.

[33] Kołos, personal communication.

[34] Stewart, Ph.D. Thesis, Mathematical Inst., Oxford, 1954.

[35] Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.