The Electronic Structure of Aromatic Molecules. Non-empirical Calculations on Indole, Benzofuran, Benzothiophen, and Related Hydrocarbons

By **Michael H. Palmer** * and **Sheila M. F. Kennedy**, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Ab initio calculations in a gaussian orbital basis (LCGO) are reported for naphthalene, indene, styrene, indole, benzofuran, and benzothiophen. A bond energy analysis on small non-aromatic molecules yields energies for the classical Kekulé structures; the resonance energies derived for the real molecules, in close agreement with figures based upon thermochemical data, are: naphthalene 357, indene 225, styrene 208, indole 308, benzofuran 232, benzothiophen 183, benzene 212 kJ mol^{-1}. The calculated dipole moments are in reasonable agreement with experiment, and are separated into σ- and π-components. The high values of the π-moments, and the degree of scatter of the π-electrons into isolated pairs are related to aromatic character. Although the molecules are not isoelectronic, extensive correlation of the orbitals in the series can be achieved, and the He$^{\text{I}}$ photoelectron spectra are interpreted in terms of the main groups of orbital energies.

PREVIOUSLY we reported non-empirical MO calculations of the ground states of various five- and six-membered monocyclic, potentially aromatic, systems containing one or more of the heteroatoms nitrogen, oxygen, phosphorus, or sulphur.[1-9] The benzo-derivatives of the five-membered ring heterocycles are of particular interest owing to the existence of the Kekulé-like and quinonoid

---

[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, *Theor. Chim. Acta*, 1972, **26**, 357.

[3] S. Cradock, R. H. Findlay, and M. H. Palmer, *Tetrahedron*, 1973, **29**, 2173.

[4] M. H. Palmer, A. J. Gaskell, and R. H. Findlay, *Tetrahedron Letters*, 1973, 4659.

[5] M. H. Palmer and R. H. Findlay, *Tetrahedron Letters*, 1974, 253.

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

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

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

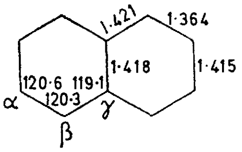
[9] M. H. Palmer, R. H. Findlay, and A. J. Gaskell, *J.C.S. Perkin II*, 1974, 778.

series; in this paper we report results on the ground states of the former series, and compare them with some related aromatic hydrocarbons.

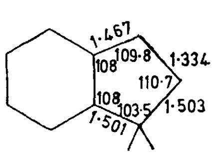
METHODS

Geometries.—The naphthalene calculation used the experimental[10] geometry (1); indene (2) was constructed from one half of naphthalene and fragments of propene,[11a] while styrene (3) was obtained similarly from the benzene[11b] and ethylene[11c] geometries. The simplest derivative of the indole system for which a geometry has been reported is the 3-acetic acid (4);[12] the carbocyclic rings of (1) and (4) differ significantly and the pyrrole portion of (4) has a significantly shorter C(2)—C(3) bond than that of pyrrole. Whilst the fusion of five- and six-membered rings may well produce these effects, the possibility that the ring system of the derivative (4) might be distorted relative to the parent molecule as a result of the 3-acetic acid group polarity could not be excluded. Furthermore, we needed to construct geometries for benzo-furan and -thiophen for which there are no reported experimental structures. Various groups of workers[13–17] have calculated bond lengths for (1) and (5)—(7) based upon self-consistent bond order (p_{ij})–bond length (r_{ij}) relationships by the equation $r_{ij} = A - Bp_{ij}$ where A and B are empirical parameters based upon ethylene, benzene *etc.*[18] These calculations do not lead to values for the bond angles, and hence are insufficient for the present work; for naphthalene most groups[13a,14,16a] calculate lengths that are in substantial agreement with the various experimental values, except that the $C_{\alpha\beta}$ bond is always calculated to be slightly too long. None the less the same series of calculations suggest that the carbocyclic parts of (5)—(7) are probably very similar to those of naphthalene (1).[*] Thus it seems reasonable to use the experimental geometric parameters from naphthalene for much of the geometry of (5)—(7); furthermore this has the added computational advantage that many electron repulsion integrals, which form the bulk of the computation time, could be used in several calculations. It is well established that INDO semiempirical calculations of total energy reproduce differences in geometric features fairly well. Thus as a final check we carried out two INDO calculations of the indole system using (a) the 3-acetic acid geometry (4) and (b) the geometry (5) based upon the superposition of pyrrole and one half of naphthalene. The total energies were (4) −71·2020 and (5) −71·2616 a.u. *Overall* geometry (5) appears slightly better than (4); thus we chose to use (5) and constructed the corresponding ones (6) and (7), by the same procedure from furan and thiophen and naphthalene.

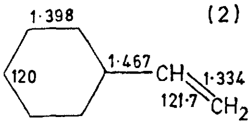
The Gaussian Basis.—The linear combination of *scaled* ' best atom ' gaussian functions (GTOs) consisted of five, two, three, and three GTOs for $1s_X$, $2s_X$, $2p_X$ (where X = C, N, and O) and $1s_H$ respectively, while sulphur was represented by six, two, two, four, two, and one GTOs for $1s$, $2s$, $3s$, $2p$, $3p$, and $3d$ respectively. The scaling procedures, based upon ethylene, vinyl alcohol, vinylamine[2,6] and thioformaldehyde,[†] are optimal in total energy for contraction of this basis to the above orbitals. As before we define the heat of atomisation (binding energy) to be the difference between the total molecular energy using the *scaled* basis, and the atom sum using the *best atom* basis. The free atom energies (a.u.) using the unscaled basis, the Hartree–Fock limit,[19] and the percentage of the latter are: H (^2S), −0·4970, −0·5000 (99·4); C (^3P), −37·6105, −37·6886 (99·8); N (^4S), −54·2754, −54·4009 (99·8); O (^3P), −74·6121, −74·8094 (99·7); S (^3P), −396·7476, −397·5048 (99·8). The computations were executed with the ATMOL-2 system of programs on an IBM370/195 computer, and the main results are shown in Tables 1—4.



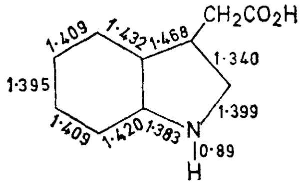
(1)



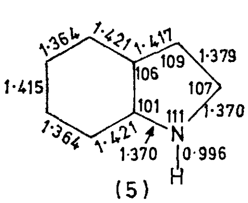
(2)



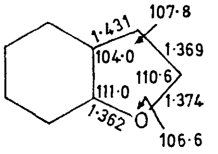
(3)



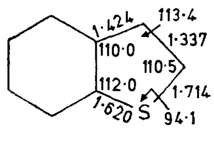
(4)



(5)



(6)



(7)

---

[*] Errors in these calculations are usually ±0·02 Å, but are often better for selected bonds within each molecule.

[†] The best total energy for thioformaldehyde was −435·6818 (*spd* basis with the optimum 3*d* exponent of 0·540). The best *sp* basis result was −435·5946 a.u.

[10] A. Acmenningen, O. Bastiansen, and F. Dyvik, *Acta Cryst.*, 1961, **14**, 1056.

[11] (*a*) D. R. Lide and D. Christensen, *J. Chem. Phys.*, 1961, **35**, 1374; (*b*) G. E. Bacon, N. A. Curry, and S. A. Wilson, *Proc. Roy. Soc.*, 1964, *A*, 279, 98; (*c*) L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, 1964, **42**, 2683.

[12] I. A. Karle, K. Britts, and P. Gum, *Acta Cryst.*, 1964, 496.

[13] (*a*) F. Momicchioli and A. Rastelli, *J. Mol. Spectroscopy*, 1967, **22**, 310; (*b*) C. Aussems, S. Jaspers, G. Leroy, and F. Van Remoortere, *Bull. Soc. chim. belges*, 1969, **78**, 479.

[14] M. J. S. Dewar and N. Trinajstic, *J. Chem. Soc.* (*A*), 1971, 1220; M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, 1966, **44** 759; M. J. S. Dewar, A. J. Harget, N. Trinajstic, and S. D Worley, *Tetrahedron*, 1970, **26**, 4505.

[15] N. Trinajstic and A. Hinchcliffe, *Z. phys. Chem. Neue Folge*, 1968, **59**, 271; L. Klasinc, E. Pop, N. Trinajstic, and J. V. Knop, *Tetrahedron*, 1972, **28**, 3465.

[16] (*a*) J. Fabian, A. Mehlhorn, and R. Zahradnik, *J. Phys. Chem.*, 1968, **72**, 3975; (*b*) A. Skancke and P. N. Skancke, *Acta Chem. Scand.*, 1970, **24**, 23.

[17] (*a*) R. A. Sallavanti and D. D. Fitts, *Internat. J. Quant. Chem.*, 1969, **3**, 33; (*b*) G. Favini and A. Gamba, *J. Chim. Phys.*, 1967, **64**, 1443.

[18] C. A. Coulson and A. Golebiewski, *Proc. Phys. Soc.*, 1961, **78**, 1310.

[19] E. Clementi, ' Tables of Atomic Functions,' Supplement to IBM J. Research and Development, 1965, vol. 9, p. 2.

TABLE 1

Molecular energies for the systems

	Naphthalene	Indene	Styrene	Indole
Total energy (a.u.) [a]	−382·37127	−344·58111	−306·79044	−360·52655
Binding energy (a.u.)	−2·29027	−2·11071	−1·93044	−1·88815
Resonance energy (calc) (kJ mol^{-1})	357	225	208	308
Resonance energy (thermochemical) (kJ mol^{-1})	314		176	226
	Benzofuran	Benzothiophen (*sp* basis)	Benzothiophen (*spd* + 3s′ basis)	Benzene
Total energy (a.u.)	−380·26093	−702·32203	−702·44606	−230·11426
Binding energy (a.u.)	−1·78283	−1·70843	−1·83246	−1·46945
Resonance energy (calc) (kJ mol^{-1})	232	242	283	212
Resonance energy (thermochemical) (kJ mol^{-1})				155

[a] Energy conversion units (see ' Symbols, Signs and Abbreviations,' the Royal Society, London, 1969) are 1 a.u. = 2625·46 kJ mol^{-1}, 1 a.u. = 27·211 eV, 1 eV = 1·6021 × 10^{-19} J.

TABLE 2

Molecular and derived bond energies (a.u.) from non-aromatic compounds

CH_4	−40·10176	C_2H_4	−77·83154	$(CH_2{=}CH)_2$	−154·50920		
CH	−10·0254	C=C	−37·7296	C_{sp^2}–C_{sp^2}	−18·8972		
$CH_2{=}CHOH$	−152·46202	$CH_2{=}CHNH_2$	−132·54130	NH_3	−56·01986	H_2S(*sp*)	−397·84420
C_{sp^2}–O	−46·7561	C_{sp^2}–N	−27·5378	NH	−18·6733	SH(*sp*)	−198·9221
$CH_2{=}CHSH$(*sp*)	−474·51823	$CH_2{=}CHSH$(*spd*)	−474·61525	H_2O	−75·79988	H_2S(*spd*)	−397·94040
C_{sp^2}–S	−207·7848	C_{sp^2}–S(*spd*)	−207·8391	OH	−37·8999	SH(*spd*)	−198·9702

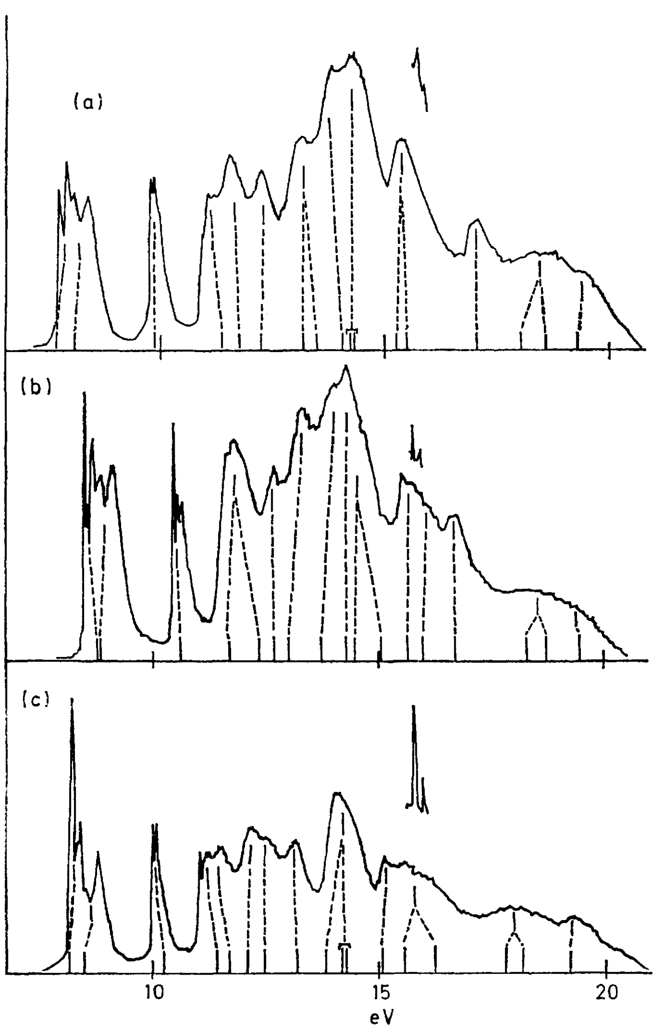


FIGURE 1 He^{I} Photoelectron spectra of (a) indole, (b) benzofuran, and (c) benzothiophen

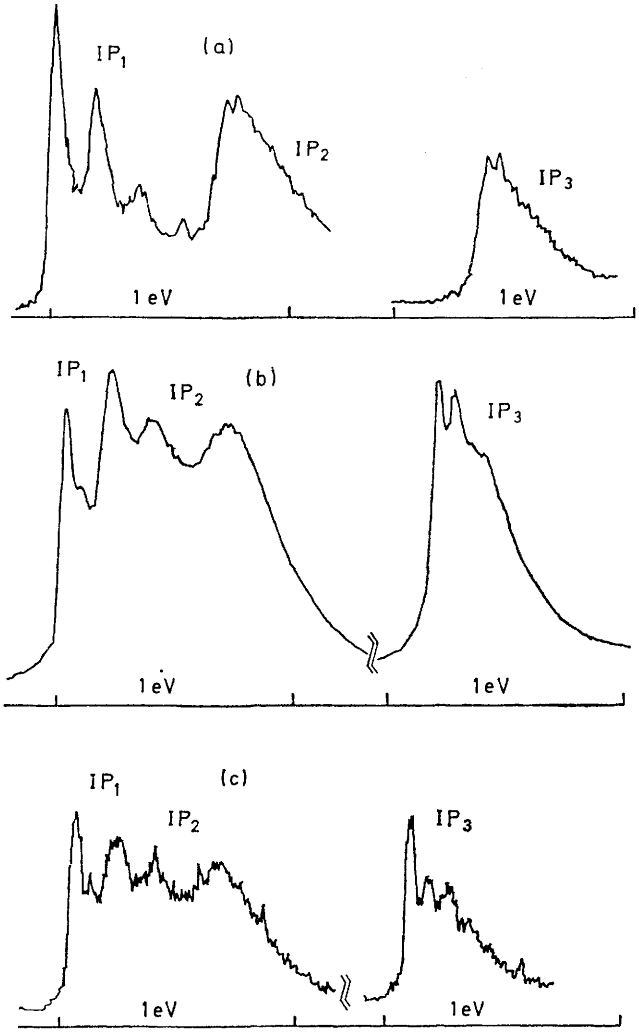


FIGURE 2 Expansion (×5) of He^{I} photoelectron spectra of (a) naphthalene, (b) indole, and (c) benzofuran

EXPERIMENTAL

The title compounds were purified by vacuum sublimation, except for benzofuran which was fractionally distilled. The photoelectron spectra using He^{I} irradiation were obtained using a Perkin-Elmer PS16 spectrometer and were calibrated with the argon doublet at 15·75 and 15·93 eV (inset in Figure 1). Expansions (×5) of the bands where appreciable fine structure is evident are shown in Figure 2. The band assignments in Figure 1 are based upon the calculated orbital energies using Koopmans' theorem. Condensed phase (−150°) studies of the electron energy levels were obtained using an A.E.I. ES200 (by courtesy of A.E.I. Scientific Apparatus Division) and were calibrated with the acetone $1s_{O}$ doublet; the valency shell spectra were generally poorly defined under these conditions, but that from benzofuran (Figure 3) allows identification of the principal 2*s* groupings.

TABLE 3

Molecular orbital energy levels (eV) of naphthalene

a_{1g}	Character [a–c]
−307·3	$1s_{\gamma}$
−306·8	$1s_{\beta}$
−306·8	$1s_{\alpha}$
−32·33	$2s_{\alpha+\beta+\gamma}$
−27·56	$2s_{\beta-\gamma}$
−22·31	$(2p + 1s_{H})_{\alpha}$ (T)
−18·78	$(2p + 1s_{H})_{\beta}$ (L)
−17·14	$2p$ (L + T)
−13·17	$(2p + 1s_{H})_{\alpha} + 2p_{\beta}$ (T)

b_{3g}	Character
−11·29	$2p_{\alpha+\beta+\gamma}$

b_{1g}	Character [a–c]
−306·9	$1s_{\beta}$
−306·8	$1s_{\alpha}$
−26·94	$2s_{\alpha+\beta}$
−19·18	$(2p + 1s_{H})_{\beta}$ (L)
−16·30	$(2p + 1s_{H})_{\alpha}$ (T)
−13·44	$(2p + 1s_{H})_{\beta}$ (L)

b_{3u}	Character [a–c]
−306·8	$1s_{\beta}$
−306·8	$1s_{\alpha}$
−30·48	$2s_{\alpha+\beta}$
−23·27	$2s_{\alpha-\beta} + 2p + (2p + 1s_{H})_{\beta}$
−19·54	$(2p + 1s_{H})_{\alpha+\beta}$
−16·24	$2p_{\alpha-\beta+\gamma}$ (L)
−14·48	$2p_{\alpha-\beta}$ (T)

b_{2u}	Character [a–c]
−307·3	$1s_{\gamma}$
−306·8	$1s_{\beta}$
−306·8	$1s_{\alpha}$
−28·73	$2s_{\alpha+\beta+\gamma}$
−22·88	$2p$ (L + T)
−17·12	$(2p + 1s_{H})_{\alpha}$ (T)
−15·54	$(2p + 1s_{H})_{\beta} + 2p_{\alpha}$ (L)

b_{1u}	Character [a,c]
−15·48	$2p_{\alpha+\beta+\gamma}$
−9·47	$2p_{\beta-\gamma}$

b_{2g}	Character [a,c]
−13·09	$2p_{\alpha+\beta}$

a_{1u}	Character [a,b]
−8·57	$2p_{\alpha+\beta}$

[a] Allowable combinations of orbitals within the symmetry representation, where the positions are α: 1, 4, 5, 8; β: 2, 3, 6, 7; γ: 4a, 8a. [b] CH and CC bonds of largely longitudinal character, *i.e.* parallel to the long axis of the molecule are labelled L; those of transverse character and parallel to the short in-plane symmetry axis are labelled T. [c] The molecule lies in the *yz* plane with the *z*-axis as the long axis. The D_{2h} symmetry nomenclature follows ref. 35.

TABLE 4

Molecular orbital energy levels (eV) for styrene, indene, indole, benzofuran, and benzothiophen

Styrene

a′ (σ)

−307·2, −306·8, −306·8, −306·8, −306·8, −306·8, −306·7, −306·2, −31·70, −29·31, −27·69, −26·91, −23·14, −22·39, −20·84, −19·44, −18·02, −17·20, −16·93, −16·26, −15·94, −14·50, −13·56, −13·33

a″ (π)

−14·82, −11·93, −9·84, −8·88

Indene

a′ (σ)

−306·8, −306·8, −306·7, −306·7, −306·6, −306·6, −306·6, −306·5, −306·4, −32·25, −30·25, −27·88, −26·47, −25·72, −22·48, −21·45, −20·49, −18·70, −17·86, −17·07, −16·26, −16·05, −14·86, −13·93, −13·76, −12·87

a″ (π)

−16·89, −14·12, −11·61, −9·61, −8·58

Indole

a′ (σ)

−402·9, −307·9, −307,6, −306·7, −306·5, −306·5, −306·5, −306·3, −305·8, −35·24, −30·90, −28·69, −27·26, −26·60, −23·01, −21·98, −21·42, −20·13, −18·22, −17·96, −16·60, −16·36, −15·67, −15·24, −14·06, −12·99

a″ (π)

−16·73, −13·46, −11·08, −8·83, −8·20

Benzofuran

a′ (σ)

−561·4, −309·4, −308·9, −307·4, −307·3, −307·3, −307·2, −307·1, −307·0, −39·1, −31·76, −29·68, −27·89, −27·34, −23·35, −22·34, −19·78, −18·88, −18·41, −16·92, −16·68, −16·00, −15·06, −14·66, −13·30

a″ (π)

−17·66, −14·21, −11·98, −9·67, −9·16

Benzothiophen (*spd* + 3*s′* basis)

a′ (σ)

−2495, −307·7, −307·4, −307·2, −307·1, −307·0, −307·0, −306·9, −306·8, −238·1, −180·7, −180·6, −33·14, −30·72, −28·58, −27·10, −26·37, −23·03, −21·71, −21·22, −19·17, −18·30, −17·68, −16·64, −16·52, −15·28, −14·32, −13·87, −12·97

a″ (π)

−180·55, −16·07, −13·32, −11·46, −9·21, −8·76

DISCUSSION

(a) *The Molecular Energies.*—The present calculation on naphthalene (Table 1) using 184 GTOs yields a total energy very similar to that of the 290 gaussian lobe function calculation by Buenker and Peyerimhoff,[20] but 54 a.u. better than the only other 'all electron' calculation,

---

[20] R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Letters*, 1969, **3**, 37.

using floating spherical gaussian orbitals.[21,*] The present styrene calculation is *ca.* 3·0 a.u. better than an earlier GTO minimal basis calculation;[22] no *ab initio* calculations on the molecules (2) and (5)—(7) have been reported previously.

A study of the eigenvectors in the benzothiophen calculations with and without 3*d* orbitals suggests that the role of the latter is that of polarisation functions rather than as strongly bonding orbitals, since in all cases the 3*d* eigenvectors are very low ($<0·1$). It is necessary to use six, rather than the usual five, 3*d* functions in LCGO calculations; this allowed a clear differentiation of the roles of polarisation functions. The six functions were contracted[23] to the usual group of five ($3d_{x^2-y^2}$, $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{z^2}$), the *spd* basis, and a further *s*-type function ($3s' \equiv 3d_{x^2+y^2+z^2}$). Selective use of these in the SCF procedure led to the following results for total energy (and dipole moment): *sp* basis $-702·32203$ (1·37), $sp + 3s'$ basis $-702·36890$ (1·37), *spd* basis $-702·39913$ (0·56), $spd + 3s'$ basis $-702·44606$ a.u. (0·56 D); it is clear that a single $3s'$ function leads to a much larger increment in total energy (0·0469 a.u.) than that for a 3*d* function (0·0154 a.u.) (*cf.* refs. 6 and 8). Thus the angular properties of the 3*d* funtions are of little value except to lead to minor readjustments of the electron distribution, as evidenced by the improvement in the dipole moment (experimental 0·62 D).

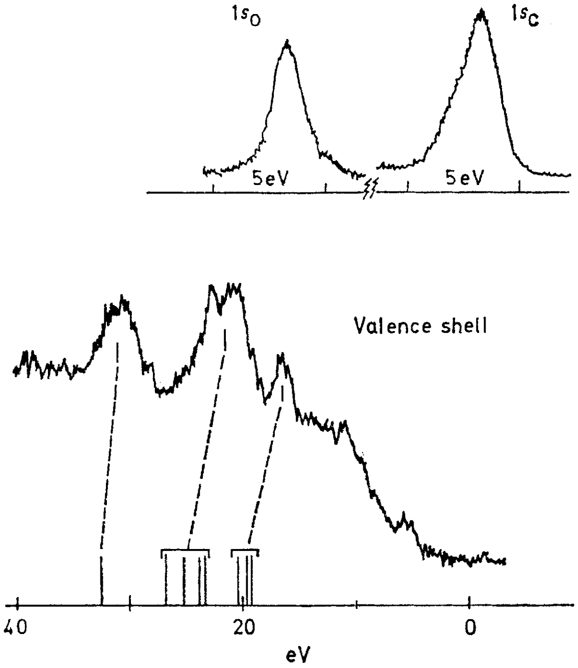


FIGURE 3 *X*-Ray photoelectron spectra of benzofuran

The binding energy series (Table 1) is similar in the monocyclic and benzo-derivatives, benzene,[24] pyrrole,[1,2] thiophen (*spd*),[6] and furan [1,2] having values 1·469, 1·060, 1·061, and 0·440 a.u. However, a more sensitive insight into the interaction of the rings and the degree of aromatic character is provided by the estimated resonance energies. The procedure is based upon partition of the *total* energy of selected molecules into bond contributions. In this way the correlation error, which leads to low bond energies on the usual thermochemical scale, is largely eliminated since the largest terms in the correlation energy are the intrabond pair correlation energies. The total energy of all the fragment molecules (Table 2) is calculated with an *identical* basis set; the contributon E_{C-H} is then $\frac{1}{4}E_{CH_4}$, and this figure inserted into the ethylene energy ($E_{C_2H_4}$) yields $E_{C=C}$; the problem of identifying the value of E_{C-C} between sp^2–sp^2 carbon atoms which is a fundamental problem with thermochemical studies is solved from inserting the above values E_{C-H} and $E_{C=C}$, into the total energy of twisted buta-1,3-diene where the π-orbitals are perpendicular and hence non-interacting. Similar procedures with ammonia, water, and hydrogen sulphide lead to E_{N-H}, E_{O-H}, and E_{S-H}; these data inserted into the computations on vinylamine, vinyl alcohol, and ethylenethiol where the protons are rotated out of plane to remove the π–π lone pair–vinyl group interaction yield values of E_{C-X} where X = N, O, and S. The bond and total energies of the fragment molecules are given in Table 2.

We now adopt the original definition [25,26] of resonance energy (RE), namely that it is the difference in total energy between the molecule (calculated or experimental) and that of the classical molecule with non-interacting olefinic and saturated systems, whose total energy is derived from the sum of the bond contributions.† The procedure yields a linear correlation with Pauling's[26] thermochemical mesomeric energies (ME) with the form

---

* The orbital ordering (Table 3) for naphthalene is virtually identical in all three calculations, with only minor changes where near degenerate levels occur ($5b_{3u}$ and $4b_{1g}$, $8a_{1g}$, and $6b_{2u}$). It is worth noting that for a wide range of aromatic and heterocyclic compounds the differences in orbital ordering between minimal and double zeta bases are insignificant.[9] This leads to confident assignments of the major groupings of the photoelectron spectra from these minimal basis calculations.

† The alternative definition introduced by Dewar[27] that the resonance energy becomes the difference in heat of atomisation between a given conjugated hydrocarbon and the value calculated for a corresponding classical (open chain) polyene by summing the appropriate bond energies, is very appealing in certain ways. It suffers from the disadvantage that (a) it assumes that polyolefinic systems have no resonance energy (*cf.* above), (b) no acyclic molecule can have any aromaticity, (c) the definition fails with cyclic systems where a saturated centre intervenes in the conjugation (as for example with cyclopentadiene). Clearly the latter could be used as an alternative to buta-1,3-diene in determining the energy of C_{sp^2}–C_{sp^2}.

[21] R. E. Christoffersen, *J. Amer. Chem. Soc.*, 1971, **93**, 4104; R. E. Christoffersen, D. W. Genson, and G. M. Maggiora, *J. Chem. Phys.*, 1971, **54**, 239.

[22] W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496.

[23] A. Rauk and I. G. Csizmadia, *Canad. J. Chem.*, 1968, **46**, 1205.

[24] M. H. Palmer and W. Moyes, to be published; M. H. Palmer and J. Nisbet, to be published.

[25] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1969, p. 220.

[26] L. Pauling, 'The Nature of the Chemical Bond,' Cornell Univ. Press, New York, 1960, 3rd edn., pp. 190 *et seq.*

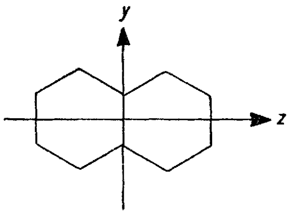
[27] M. J. S. Dewar, A. J. Harget, and N. Trinajstic, *J. Amer. Chem. Soc.*, 1969, **91**, 6321.

ME = 0·874RE − 4·47 kJ mol^{-1}.* The difference in energy between the planar and non-planar vinylamine (37), ethylenethiol (14), and vinyl alcohol (10 kJ mol^{-1}) is sufficiently large for this not be to classified as a rotation barrier but rather as resonance energy. The data for the present molecules (Table 1) seem reasonable when compared with those for benzene (212), pyrrole (149), furan (89), and thiophen (no *d* orbitals 124, with *d* orbitals 144 kJ mol^{-1}); thus naphthalene is rather less aromatic than twice benzene; styrene and indene are near to that for benzene, while the bicyclic heterocycles are substantially less than that of the monocyclic heterocycle plus benzene.† This last point is in accord with the even higher vinyl character in the C(2)–C(3) bond of the bi- than the mono-cyclic systems.

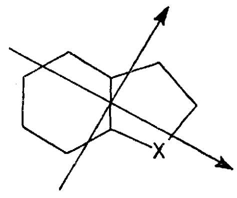
Many authors have proposed values for the resonance energies of simple benzenoid hydrocarbons and the heterocycles [*e.g.* (5)—(7)]; most of these values are either based upon thermochemical data [25,26] or calculations of an empirical or semiempirical type. Here we note that Dewar's definition of resonance energy,[27] when applied within the PPP π-electron framework [28,29] together with α-bond energy estimates, or within a revised Hückel framework [30-32] where values for the C_{sp^3}–C_{sp^2} single and double bond energies are included, leads to parallel results to the present work. Indeed these last two methods are related in a least squares fit ‡ by HMO = 0·485(PPP) + 12·35 kJ mol^{-1} with standard deviations in slope, intercept, and overall of 0·032, 0·991, and 1·464, respectively. In the same way Dewar's data are related to Pauling's [26] by PPP = 0·494ME − 15·32 kJ mol^{-1} with deviations (as above) of 0·062, 4·40, and 5·467 respectively.‡

(b) *The MO Energy Levels.*—The core $1s_C$ levels are characterised by eigenvectors >0·98 (as are those of $1s_N$, $1s_O$ *etc.*) and are spread over a very small energy range. In all the bicyclic systems the bridging carbon atoms $1s_C$ are at highest binding energy. For naphthalene the only case where experimental data are available, the *X*-ray photoelectron spectrum [33] order is again $1s_{\gamma C} > 1s_{\alpha C} > 1s_{\beta C}$; since the LCGO method usually magnifies [2,3,7,8,34] the separation of $1s_C$ levels, it seems like that the deconvolution technique of ref. 33 is leading to an artificially large separation. Even so the very small shift in $1s_C$ levels in (1) and (3) is a substantial verification of the postulated lack of charge separation in alternant hydrocarbons.

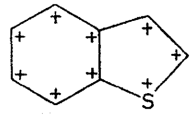
The inner valency shell orbitals (27—35 eV) in the hydrocarbons are linear combinations of $2s_C$ orbitals, and all of (1), (3), and (5)—(7) show five such levels where one is largely N(5), O(6), or S(7) in the heterocycles. Above this lies a further separate group of three largely $2s_C$ levels (22—24 eV) which persist through the group (1), (5)—(7), but are more diffuse in (2), and are joined in (3) by a further 2*s* level absent in the inner valency shell region. The outer valency shell region is largely combinations of $2p_{C(N,O)}$ or $3p_S$ mixed with $1s_H$ and some loss of similarity in the spectra of (1)—(3) and (5)—(7) is apparent. However, a further classification of the valency shell σ-orbitals into those in which the constituent dominant atomic orbitals are either parallel to or transverse to the long molecular axis (8) is possible. We have previously noted that a similar classification into this longitudinal (L) and transverse (T) character can be done with many heterocycles.[3] In naphthalene, $4b_{1g}$ for example consists of $C_\alpha C_\beta + C_\alpha C_\gamma + C_\beta H_\beta$ bonding by orbitals parallel to the long (*z*) axis (longitudinal polarisation), while $6b_{3u}$ is largely $C_\alpha C_\beta + C_\alpha C_\gamma$ bonding. Typical examples of orbitals of transverse (T) character in which the dominant $2p_C$ orbitals are parallel to the transverse in-plane (*y*) axis are $6b_{2u}$ ($C_\alpha H_\alpha$ bonding) and $7b_{3u}$ ($C_\beta C_\beta$ bonding with rather less $C_\alpha H_\alpha$ bonding). Comparatively few orbitals are of mixed L + T character (Table 3), and these are of entirely radial or tangential character with respect to the individual rings; examples



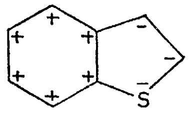
(8)



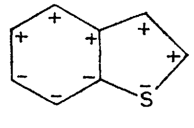
(9)



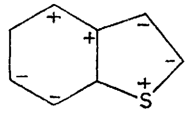
(10) ($14a'$, a_g)



(11) ($15a'$, b_{3u})



(12) ($16a'$, b_{2u})



(13) ($17a'$, b_{1g})

---

* Based upon data for benzene, naphthalene, anthracene, phenanthrene, cyclo-octatetraene, butadiene, ethylene, furan, pyrrole, thiophen, styrene, and indole; standard deviations in slope, intercept, and overall are 0·028, 1·823, and 3·876.

† An indication that these figures are not greatly effected by the basis set is afforded by similar results using the best atom basis [1] for the non-aromatic species (*cf.* Table 2) which lead to resonance energies for benzene (180), pyrrole (150), and furan (78 kJ mol^{-1}) respectively.

‡ Based upon figures for benzene, naphthalene, anthracene, phenanthrene, furan, pyrrole, and indole.

[28] M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, 1969, **91**, 789.

[29] M. J. S. Dewar, A. J. Harget, N. Trinajstic, and S. D. Worley, *Tetrahedron*, 1970, **26**, 4505.

[30] B. A. Hess and L. J. Schaad, *J. Amer. Chem. Soc.*, 1971, **93**, 305.

[31] B. A. Hess, L. J. Schaad, and C. W. Holyoke, *Tetrahedron*, 1972, **28**, 3657.

[32] B. A. Hess and L. J. Schaad, *J. Amer. Chem. Soc.*, 1973, **95**, 3907.

[33] D. T. Clark and D. Kilcast, *J. Chem. Soc.* (*B*), 1971, 2243.

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

are $5b_{3u}$ and $8a_{1g}$ which are analogous to the radial and tangential orbitals b_{1u} and b_{2u} of benzene. The molecular orbitals of (2) and (5)—(7) show an apparent ' symmetry axis ' as in (9), and are largely polarised longitudinally or transversely with respect to this axis. Of course the eigenvectors are not equal in magnitude across these ' symmetry axes ' as they are in naphthalene. Typical examples of these correlations are shown (10)—(13) for the $2s_O + 3s_S$ levels of benzothiophen with the corresponding naphthalene orbitals in parentheses. By the use of this property we are able to correlate many of the orbitals (Figure 4). Styrene again shows rather different properties, and is clearly closer to a combination of benzene and ethylene than to indene or the other compounds.

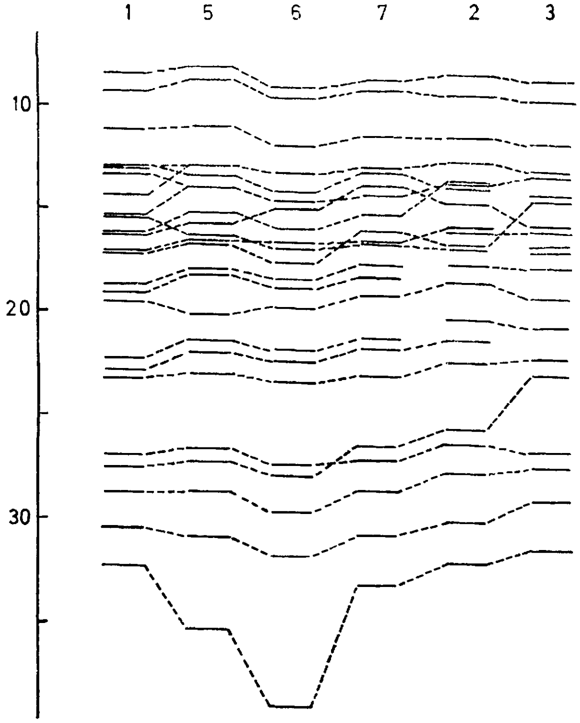


FIGURE 4 Correlation diagram for molecules (1)—(3) and (5)—(7)

The comparatively small number of changes in orbital ordering in the series (1), (3), (5)—(7) is a reflection of the great similarity in electronic structure in the series. This is reflected in their electronic [35,36] and photoelectron spectra [37-42] also. Most of the cross-overs in Figure 4 can can be attributed to changes in the free atom orbital energies, of which relevant ones in the Hartree–Fock limit are: 2*s*: C, 19·2; N, 25·7; O, 33·9; 2*p*: C, 11·8; N, 15·4; O, 17·2; 3*s*: S, 23·9; 3*p*; S, 11·9 eV. Thus the similarity of benzothiophen to naphthalene is also the most marked on this basis as well as in resonance energy (see also below).

The correlation of the π-orbitals in the series is the most marked. The simplified MO treatment of naphthalene in which it is treated as a ten-membered ring polygon,[36] and much used in the Platt method of analysis of electronic spectra [35,36] is not far from correct. The separation of the orbital pairs concerned (b_{1u}, a_{1u}), (b_{2g}, b_{3g}) is 0·9 and 1·8 eV respectively.

(c) *The Photoelectron Spectra. Assignments using the Orbital Energies.*—The He^{I} [37-43] spectra of the compounds (1)—(6) have been recorded previously and this has been extended to He^{II} for (1) and (3),[43] but interpretation has either been limited to postulated π-levels supported by Hückel,[37,41] SPINDO/1,[43] EHT, and PPP semiempirical calculations [40] or the effects of perfluorination.[42] The almost complete separation of π- and σ-levels observed in the present calculations (Table 3 and 4) offers a reprospective justification of the assignments based upon the Hückel method.

TABLE 5

Assignment of vertical IPs to orbital energies ε_i (eV) for hydrocarbons (1)—(3)

Naphthalene								
IP	8·3	8·95	10·5	11·05	11·4	11·85	12·5	13·5
$-\varepsilon_i$	8·57	9·47	11·29	13·09	13·17	13·44	14·48	15·48/15·54
IP	14·0	14·45	15·85	16·4	18·8	22·1		
$-\varepsilon_i$	16·24/16·30	17·12/17·14	18·78	19·18/19·54	22·31/22·88/23·27	26·94/27·56/28·73		
Indene								
IP	8·2	8·95	10·35	11·58	12·0	12·9		
$-\varepsilon_i$	8·58	9·61	11·60	12·87	13·76/13·93/14·12	14·86		
IP	13·6	15·0	16·1	18·0				
$-\varepsilon_i$	16·05/16·26	16·89/17·07	18·07	20·49/21·45/22·48				
Styrene								
IP	8·55	9·25	10·55	11·6	12·2	12·7	13·7	
$-\varepsilon_i$	8·88	9·84	11·93	13·33	13·56	14·5/14·82	15·93/16·26	
IP	15	15·5		16·6	17·85	18·9	19·35	22·3
$-\varepsilon_i$	16·93/17·20		18·02	19·44	20·84	22·39	23·14	26·91/27·69

---

[35] H. H. Jaffe and M. Orchin, ' Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, p. 294.

[36] J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 484.

[37] J. H. D. Eland and C. J. Danby, *Z. Naturforsch.*, 1968, **23a**, 355.

[38] J. H. D. Eland, *Internat. J. Mass Spectroscopy Ion Phys.*, 1969, **2**, 471.

[39] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, ' Molecular Photoelectron Spectroscopy,' Wiley-Interscience, London, 1970.

[40] P. A. Clark, R. Gleiter, and E. Heilbronner, *Tetrahedron*, 1973, **29**, 3085.

[41] P. A. Clark, F. Brogli, and E. Heilbronner, *Helv. Chim. Acta*, 1972, **55**, 1415.

[42] C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, 1972, **94**, 1466.

[43] E. Lindholm, C. Fridh, and L. Asbrink, *Discuss. Faraday Soc.*, 1972, **54**, 127.

TABLE 6

Assignment of vertical IPs to orbital energies ε_i (eV) for heterocycles (5)—(7)

Indole									
	IP	7·79	8·18	9·88	11·12	115·6	12·24	13·26	
	$-\varepsilon_i$	8·20	8·83	11·08	12·99	13·46	14·06	15·24/1567	
	IP	13·77	14·28	15·40	17·03	18·51			
	$-\varepsilon_i$	16·36	16·60/16·73	17·96/18·22	10·23	21·98/23·01			
Benzofuran									
	IP	8·66	8·94	10·58	11·83	12·67	13·31	14·01	14·31
	$-\varepsilon_i$	9·16	9·67	11·98	13·30/14·21	14·66	15·06	16·00	16·68
	IP	14·54	15·69	16·09	16·69	185·4	19·39		
	$-\varepsilon_i$	16·92/17·66	18·41	18·88	19·78	21·82/22·34	23·47		
Benzothiophen									
Basis	IP	8·75	8·75	10·07	11·20	11·45	12·15	12·45	13·10
spd + 3*s*′	$-\varepsilon_i$	8·76	9·21	11·45	12·97	13·32	13·87	14·32	15·28
sp	$-\varepsilon_i$	9·00	9·44	11·67	12·84	13·51	13·96	14·44	15·36
	IP	14·25	15·20	15·80	17·98	19·27			
spd + 3*s*′	$-\varepsilon_i$	16·07/16·52/16·64	17·68	18·30/19·16	21/22·21/71	23·03			
sp	$-\varepsilon_i$	16·35/16·75/16·76	17·75	18·43/19·35	21·35/21·83	23·23			

TABLE 7

Vibrational frequencies excited in the photoelectron spectra (cm^{-1}) (neutral ground state modes in parentheses)

	IP_1	IP_2	IP_3
Naphthalene	1400 (1477)		1265 (1393) 390 (511)
Indole	1350 (1454) 520 (612)	2620	645 (612)
Benzofuran	1480 (1254) 580 (540)		645 (766)
Benzothiophen	1310 (1497) 850 (884)		

TABLE 8

Dipole moments (μ/D) and directions

	Total		Calculated				Observed	
	μ [a]	θ [b]	μ_σ [a]	θ [b]	μ_π [a]	θ [b]	μ	θ [b]
Styrene	0·027	51					0·13,[c]	
							0·2,[d]	
							0·181,[e]	75·8
							0·43,[f]	
Indene	0·915	49					0·85 [g]	
Indole	2·31	48	−0·44	46	2·75	231	2·08 [h]	50
Benzofuran	−1·56	8	−3·00	196	1·46	25	0·79 [i]	
Benzothiophen (*spd* + 3*s*′ basis)	−0·56	2	−2·48	247	1·99	60	0·62 [j]	

[a] The usual convention that the dipole moments of furan and pyrrole are negative and positive respectively, requires that the dipole moment is positive when the negative end lies away from the heteroatom and towards the C(3)–C(3a) bond; *i.e.* in the positive cartesian direction when the molecules are oriented as in (5)—(7). [b] Angles with respect to the C(7a)–C(3a) bond axis. The orientation is as in (5)—(7) and angles are positive anticlockwise. Styrene is positive anticlockwise with respect to the C(1)–C(α) bond axis. [c] Ref. 49. [d] Ref. 53. [e] Ref. 52. [f] Ref. 50. [g] D. V. G. L. N. Rao, *Indian J. Phys.*, 1955, **29**, 398. [h] E. F. J. Janetzky and M. C. Lebret, *Rec. Trav. chim.*, 1944, **63**, 123. [i] R. D. Brown and B. W. Coller, *Theor. Chim. Acta*, 1967, **7**, 259. [j] R. G. Charles and H. Fieser, *J. Amer. Chem. Soc.*, 1950, **72**, 2233.

In our previous work with monocyclic systems linear correlations between the calculated $\mathrm{IP_{calc}}$ and observed $\mathrm{IP_{obs}}$ of the form $\mathrm{IP_{obs}} = A\mathrm{IP_{calc}} + B$ eV had *A ca.* 0·8, whilst for a series of sulphur heterocycles, requiring rather larger bases than the present, *A ca.* 0·6 was obtained. Thus in the present work a value of *A ca.* 0·7 was anticipated, since the scale factor *A* is dependent upon basis set size. A further feature assisting in the determination of the correlation line is the large number of IPs evident in the experimental spectrum in each of (1)—(6); thus comparatively few multiple assignments to a particular part of the band envelope are necessary, and these were done on the basis of band intensity and computed groupings and in the case of (1) and (3) follow the analysis of Lindholm *et al.*[37] The results are shown in Tables 5 and 6, and in Figure 1. The final correlation lines (with standard deviations in slope and intercept, and overall standard deviation) are: naphthalene, $\mathrm{IP_{obs}} = 0{\cdot}755\mathrm{IP_{calc}} + 1{\cdot}702$ eV (0·014, 0·213, 0·190); indene, $\mathrm{IP_{obs}} = 0{\cdot}773\mathrm{IP_{calc}} + 1{\cdot}479$ eV (0·020, 0·295, 0·237); styrene, $\mathrm{IP_{obs}} = 0{\cdot}767\mathrm{IP_{calc}} + 1{\cdot}622$ eV (0·010, 0·184, 0·200); indole, $\mathrm{IP_{obs}} = 0{\cdot}794\mathrm{IP_{calc}} + 1{\cdot}051$ eV (0·010, 0·164, 0·163); benzofuran, $\mathrm{IP_{obs}} = 0{\cdot}779\mathrm{IP_{calc}} + 1{\cdot}300$ eV (0·010, 0·170, 0·152); benzothiophen (*sp* basis) $\mathrm{IP_{obs}} = 0{\cdot}776\mathrm{IP_{calc}} + 1{\cdot}235$ eV (0·010, 0·153, 0·144), (*spd* basis) $\mathrm{IP_{obs}} = 0{\cdot}774\mathrm{IP_{calc}} + 1{\cdot}370$ eV (0·011, 0·166, 0·158). No special significance can be placed upon the small variations in slope and intercept.

Short progressions are evident in some of the ionisations from π-orbitals in (1) and (5)—(7) (Table 7); we have indicated gas-phase vibrations of the neutral molecule which are excited in the electronic (hot band) or

TABLE 9

Average positions [a] of π-electrons in indole, benzofuran, and benzothiophen

Benzofuran

	π_1	π_2	π_3	π_4	π_5	Centre of [a] charge
$\bar{y}$ [a]	−1·2867	−0·0745	0·2381	−0·0011	0·0544	−0·0487
$\bar{z}$ [a]	1·6309	−1·9363	0·7317	−1·7504	0·0869	−0·499
$\bar{r}$ [b]	2·3568	1·5207	1·2021	1·3394	0·5321	

Average $\bar{r}$ 1·3902

Indole

	π_1	π_2	π_3	π_4	π_5	Centre of charge
$\bar{y}$ [a]	−0·9407	−0·1428	0·2455	−0·0145	0·1687	−0·0409
$\bar{z}$ [a]	1·5062	−2·0017	−0·0136	−1·1962	0·2546	−0·4960
$\bar{r}$ [b]	2·1612	1·5355	0·5409	0·7277	0·7550	

Average $\bar{r}$ 1·1441

Benzothiophen (*spd* + 3*s′* basis)

	π_1 [c]	π_2	π_3	π_4	π_5	π_6	Centre of charge
$\bar{y}$ [a]	−2·4818	−0·2769	−0·1485	−0·0022	0·0006	−0·3789	0·2668
$\bar{z}$ [a]	2·8419	0·5106	−1·0415	0·1393	−0·2684	−0·2024	−0·0697
$\bar{r}$ [b]	3·5092	0·4662	1·1061	0·3737	0·4794	0·2464	

Average $\bar{r}$ 0·5344

[a] Relative to the midpoint of the C(3a)–C(7a) bond as origin and *y*-axis; distances in atomic units (1 a.u. = $0·529167 \times 10^{-10}$ m).
[b] Relative to the centre of charge. [c] Localised $2p_\pi$ on sulphur.

TABLE 10

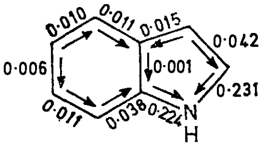
Population analyses

		C(1)	C(2)	C(4a)	H(1)	H(2)					
Naphthalene	σ	5·1381	5·1493	5·0206	0·8511	0·8506					
	π	0·9986	1·0004	1·0018							
		C(1)	C(2) or (6)	C(3) or (5)	C(4)						
Styrene	σ	5·0306	5·1353	5·1499	5·1473						
	π	1·0028	0·9996	0·9979	1·0012						
		C_α	C_β	H_α	$H_{\beta(\mathrm{cis})}$	$H_{\beta(\mathrm{trans})}$	H(2) or (6)	H(3) or (5)	H(4)		
	σ	5·1462	5·2667	0·8541	0·8588	0·8632	0·8541	0·8517	0·8518		
	π	1·0026	0·9979								
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)				
Indene	σ	5·1766	5·1429	5·1393	5·1415	5·1435	5·1426				
	π	1·1422	0·9892	1·0224	1·0086	1·0089	0·0100				
		C(7)	C(3a)	C(7a)	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)
	σ	5·0523	5·0198	5·0144	0·4409	0·8523	0·8500	0·8528	0·8528	0·8530	0·8543
	π	1·1011	1·0038	0·9900	0·4119						
		N	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(7a)		
Indole	σ	5·7891	4·9730	5·0847	5·1465	5·1283	5·1421	5·1147	4·8486		
	π	1·6585	1·0494	1·1057	0·9949	1·0356	1·0087	1·0498	1·0409		
		C(3a)	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)		
	σ	4·9914	0·6656	0·8386	0·8576	0·8526	0·8564	0·8531	0·8579		
	π	1·0562									
		O	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)			
Benzofuran	σ	6·7050	4·8486	5·1343	5·1422	5·1355	5·1503	5·1226			
	π	1·7930	1·0675	1·0331	0·9949	1·0196	0·9918	1·0308			
		C(3a)	C(7a)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)		
	σ	4·7397	4·9940	0·8124	0·8423	0·8349	0·8450	0·8433	0·8478		
	π	1·0551	1·0142								
		S	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)			
Benzothiophen (*spd* + 3*s′* basis)	σ	12·1757	5·0973	5·1298	5·1447	5·1376	5·1483	5·1215			
	π	3·7839	1·0689	1·0287	0·9928	1·0175	0·9969	1·0214			
		C(3a)	C(7a)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)		
	σ	4·9845	4·9930	0·8301	0·8429	0·8481	0·8506	0·8479	0·8480		
	π	1·0431	1·0468								

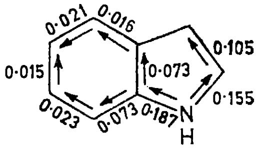
fluorescence spectra [44-46] and which are plausibly assigned to these vibrations in the ion. Only in the case of naphthalene, where a normal co-ordinate analysis has been reported,[47] is there information about the nature of the ground state molecular vibrations. The frequency ν_9 (511 cm^{-1}) in naphthalene has maximum amplitude for motion of $C_\alpha C_\beta$ relative to C_γ, *i.e.* $C_\alpha C_\gamma$ stretching; similarly ν_3 (1577 cm^{-1}) corresponds to ($C_\beta C_\beta + C_\gamma C_\gamma$) stretching +(CH) bending, ν_2 (1477 cm^{-1}) to ($C_\alpha C_\beta + C_\gamma C_\gamma$) stretching +(CH) bending, ν_4 (1393 cm^{-1}) to ($C_\alpha C_\gamma + C_\gamma C_\gamma$) stretching.[48] Ionisation from $1a_{1u}$ (IP$_1$) leads to a population decrease (—0·030e) across $C_\alpha C_\beta$ and an increase (+0·019e) across $C_\beta C_\beta$, while for $1b_{3g}$ (IP$_3$) the corresponding figures are $C_\alpha C_\beta$ (—0·018), $C_\beta C_\beta$ (+0·009), and $C_\gamma C_\gamma$ (+0·021e). Thus in the ion ν_3 should be raised, while ν_2 and ν_4 should be lowered, and we assign the frequencies as in Table 7. Firm assignments for the heterocycles (5)—(7) must await more detailed information on the nature of the molecular vibrations.

(d) *The Molecular Dipole Moments.*—Comparison of the calculated and observed magnitudes (Table 8) shows good agreement for styrene, indene, indole, and benzothiophen, but the value for benzofuran is large by 1 D (assuming correct sign). The same basis set used here for oxygen also leads to a high value (—1·01 D) for furan (expt. 0·64) whereas our earlier best atom basis gave —0·64 D for the latter.[1] Clearly optimisation in the scaling on a total energy basis reduced the optimisation in at least one molecular property. None the less, the present results and our earlier work [8] lead to unambiguous determination of dipole moment signs, and it seems likely that the higher dipole moment of benzofuran when compared with furan arises from a smaller level of π-back donation being counter balanced against the high σ-attraction; thus benzofuran is even less aromatic than furan (*cf.* resonance energies above). The data for benzothiophen and indole suggest that the ring systems are polarised in a similar fashion to the monocyclic species and thereby of somewhat higher aromatic character. The calculated angle that the dipole moment of indole makes with the molecular axes is in good agreement with that estimated from substituted indoles; [49] that for styrene differs significantly from that derived from one set of measurements,[50] but there appears to be some uncertainty in the value of this low moment.[50-53]

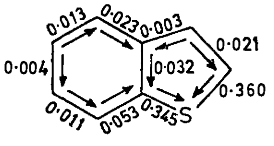
(e) *Average Positions of the π-Electrons.*—In our previous work [8] we introduced the concept that aromatic character as evidenced by a π-electron set, sextet, decet, *etc.* required that the electrons function as a group rather than as largely separate pairs. Thus their average positions ($\bar{x}$, $\bar{y}$, $\bar{z}$) from some fixed position should be (ideally) constant within the group. In some highly symmetrical molecules such as benzene this is automatically the case. In the case of the five-membered ring heterocycles C_4H_4X (X = S, NH, O, or PH) there was a progressive trend towards a quartet and a doublet, *i.e.* diene character. The average positions relative to the midpoint of the C(3a)–C(7a) bond axis for the molecules are reported in Table 9. These clearly show the increasing average distance ($\bar{r}$) in the sequence naphthalene (0·0), benzothiophen, indole, and benzofuran, which together with the resonance energies (above) follow an acceptable sequence. The distances from the centre of nuclear change, which is close to the mid-point of C(3a)–C(7a) in



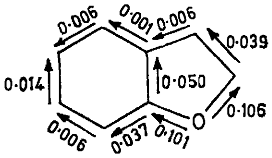
(14)(σ)



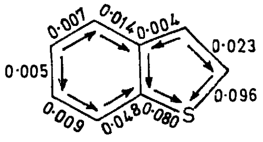
(15)(π)



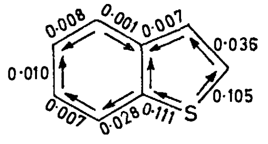
(16) (σ)



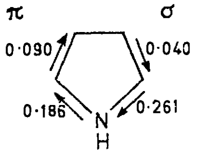
(17) (π)



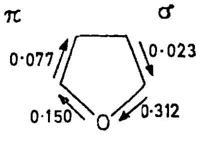
(18) (σ) (*spd* + 3*s*′ basis)



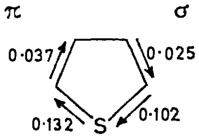
(19) (π) (*spd* + 3*s*′ basis)



(20)



(21)



(22) (*spd* + 3*s*′ basis)

---

[44] D. P. Craig, J. M. Hollas, M. F. Redies, and S. C. Wait, *Phil. Trans. Roy. Soc. A*, 1961, **253**, 543, 569.

[45] J. M. Hollas, *J. Mol. Spectroscopy*, 1962, **9**, 138; *Spectrochimica Acta*, 1963, **19**, 753.

[46] E. P. Krainov, *Optical Spectroscopy*, 1964, **16**, 415.

[47] G. Hagen and S. J. Cyvin, *J. Phys. Chem.*, 1968, **72**, 1446; S. J. Cyrin, B. N. Cyvin, and G. Hagen, *Chem. Phys. Letters*, 1968, **2**, 341.

[48] G. S. Pawley, personal communication, *cf.* G. S. Pawley and S. J. Cyvin, *J. Chem. Phys.*, 1970, **52**, 4073.

[49] H. Weiler-Feilchenfeld, A. Pullman, H. Berthod, and C. Geissner-Prettre, *J. Mol. Structure*, 1970, **6**, 297.

[50] R. A. Y. Jones, A. R. Katritzky, and A. V. Ochkin, *J. Chem. Soc.* (*B*). 1971, 1795.

[51] A. J. Petro and C. P. Smyth, *J. Amer. Chem. Soc.*, 1957, **79**, 6142; 1958, **80**, 73.

[52] J. E. Plamondon, R. J. Buenker, D. J. Koopman, and R. J. Dolter, *Proc. Iowa Acad. Sci.*, 1963, **70**, 163 (*Chem. Abs.*, 1964, **61**, 11,424a).

[53] Z. Yu. Kokoshko, V. G. Kiteava, Z. V. Pushkareva, and V. E. Blokhin, *Zhur. obshchei Zhim.*, 1967, **37**, 58.

all cases, enables a connection between the π-dipole moment and these average π-electron positions to be established. In benzothiophen all five pairs of valency π-electrons are scattered near the centre of charge. In benzofuran on the other hand, the electrons separate into a quartet near the centre of the carbocyclic ring (π_2 and π_4), one pair at the centre of charge (π_5), and pairs relatively close to the ring centre (π_3) and the oxygen atom (π_1).

(f) *Population Analyses.*—The hydrocarbons (1) and (3) show almost equal populations at the various centres, as required in the original concept of alternant hydrocarbons. In contrast the carbon σ-populations vary depending upon whether or not the atom is attached to hydrogen.

As expected the heterocycles (5)—(7) show rather larger population variations. In all cases (5)—(7) the heteroatom is a π-donor and σ-acceptor; the σ-acceptance is largely restricted to the immediately adjacent atoms C(2) and -(7a). Whilst the 3-position in (5)—(7) has a high total population, this arises more from σ- than π-polarisation, showing that the earlier π-electron theories produce the overall correct effect, but by the wrong mechanism.

As in our earlier work with monocyclic systems,[8] we have analysed the net atomic populations in terms of bond population moment contributions; full details of this method are given in ref. 8; the C–H/N–H bond contributions, immediately obvious from Table 10, are omitted as are those figures for the hydrocarbons. The carbocyclic rings (14)—(19) contain only very small bond population moments, showing that the major effects of the heteroatom are restricted to the heterocyclic ring. However, there is a small series of shifts *from* (σ) and *to* (π) the 5-position in all cases; thus the heteroatom is exerting a long range effect on a donor–acceptor basis. Comparison of the bond moments with corresponding bonds in pyrrole (20), furan (21), and thiophen (22), shows that whilst the magnitudes (σ and π) are similar in the sulphur and nitrogen compounds, they are distinctly different in benzofuran to furan. Thus the oxygen atom in (6) is a stronger σ-acceptor and poorer π-donor than in furan. These results are consistent with the varying levels of aromatic character estimated from the resonance energies above.

(g) *Conclusions.*—The *ab initio* studies reported for molecules (1)—(3) and (5)—(7) lead to satisfactory calibration of the main groups of photoelectron IPs and account for the dipole moments. The sequence of aromatic character naphthalene $>$ benzothiophen $=$ indole $>$ benzofuran $\simeq$ indene $>$ styrene is obtained from both the resonance energies and an analysis of the average position of the π-electrons. The 3*d* orbitals on sulphur in benzothiophen act primarily as polarisation orbitals and as such lead to modifications of the bonding, and as in chlorine trifluoride ' they improve but do not alter in character, the occupied MOs.'[54]

We are grateful to the S.R.C. and to the Director of the Atlas Laboratory for the provisions of computational facilities and for a grant to S. M. F. K.

[4/1204 *Received, 20th June, 1974*]

---

[54] A. Breeze, D. W. J. Cruickshank, and D. R. Armstrong, *J.C.S. Faraday II*, 1972, 1089.