The Calculation of Bond Orders, Resonance Energies, and Orbital Energies by a Simple Perturbation Method.

By M. J. S. DEWAR and R. PETTIT.

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By using the perimeter model as a basis and by considering the introduction of cross links as a perturbation, an estimate of the resonance energies, orbital energies, and bond orders of polycyclic aromatic hydrocarbons can be obtained in a much simpler manner than by the usual L.C.A.O. procedure. A linear correspondence exists for the values of the resonance energies predicted by the two methods; there is also a close agreement for the orbital-energy estimates. Some differences do occur between the two methods in the calculated bond orders and predicted bond lengths: a comparison with the experimental values for naphthalene and anthracene shows the L.C.A.O. method and the simpler new method to be about equal in the accuracy of their predictions.

THE molecular orbital method has been successfully used to account for the physical and chemical behaviour of conjugated organic molecules. Its basic conception is that the electrons of a conjugated system occupy molecular orbitals covering the entire extent of the conjugation, and in the L.C.A.O. M.O. approach the wave functions of these orbitals can be written as linear combinations of the wave functions of the various atomic orbitals involved in the conjugated system. Thus the electronic energy levels in the molecule can be determined, as well as resonance energies and bond orders. Unfortunately, in many cases, and in common with alternative methods, the straightforward L.C.A.O. M.O. treatment loses much of its appeal by virtue of the tedious calculations involved. However, it is found that, as in other branches of quantum mechanics, considerable simplification can often be introduced by use of perturbation methods. Largely because of the inclusion of perturbation methods into the M.O. theory and of the resulting simplifications a general theory has been devised which can now serve as a basis for the theoretical study of many organic compounds (Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341, 3345, 3350, 3353, 3355, 3357, and references therein; Dewar and Pettit, following paper).

It is also encouraging that in the process of simplifying the usual L.C.A.O. treatment by the inclusion of perturbation methods the validity of the results is not necessarily decreased. This fact is amply demonstrated in the calculations of the frequency of the first absorption bands of complex aromatic hydrocarbons where the predicted values given by perturbation methods are much more easily obtained and, indeed, are in far better agreement with experiment, than those obtained by the straightforward M.O. method (Dewar, *J.*, 1952, 3532).

The present paper describes how the inclusion of perturbation methods assists in the M.O. evaluation of orbital energies, resonance energies, and bond orders of polycyclic aromatic hydrocarbons; the usual M.O. calculations of these quantities are extremely tedious in such compounds, especially those having more than three fused rings and having no symmetry properties. In principle the present treatment considers a polycyclic aromatic hydrocarbon as formed by the introduction of certain cross-links into a completely conjugated cyclic polyene, *e.g.*, naphthalene is considered as formed from *cyclo*decapentaene by means of a link between $C_{(1)}$ and $C_{(6)}$. The orbital energies and bond orders of a cyclic polyene can be written down on sight and it only remains to find what effects the perturbations, *i.e.*, the introduction of the various internal cross-links, have on these values. Perimeter models have already been used by Platt (*J. Chem. Phys.*, 1949, **17**, 484) in connection with the spectra of aromatic hydrocarbons.

METHOD

Orbital Energies and Resonance Energies.—The electrons of a cyclic polyene occupy orbitals which are all doubly-degenerate, except for the lowest, which is non-degenerate. The coefficients of the wave functions of the atomic orbitals in each molecular orbital have the values $\sin n\pi x/k$ and $\cos n\pi x/k$. The wave functions of the molecular orbitals are given by :

$$\left.\begin{aligned} \Psi\,(\sin) &= \sum_{x} A \sin\,(n\pi x/k)\,.\,\psi_x \\ \text{and}\qquad \Psi\,(\cos) &= \sum_{x} A \cos\,(n\pi x/k)\,.\,\psi_x \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where ψ_x is the $2p$ A.O. of atom number x.

The energy of each of these molecular orbitals is given by

$$E = -\,2\beta \cos 2n\pi/k \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Where n is the quantum number of the orbital, k is half the total number of atoms, and A is a normalising factor having a value of $1/\sqrt{k}$ when $n \neq 0$ and $1/\sqrt{2k}$ when $n = 0$.

It will be seen that the numbering of the atoms in the polyene is purely arbitrary and to simplify the calculations it is desirable to introduce a phase factor ε such that the atomic orbital coefficients are given by the expressions :

$$A \sin\,[(n\pi x/k) + \varepsilon] \text{ and } A \cos\,[(n\pi x/k) + \varepsilon$$

No generality is lost because of this inclusion.

Now consider the formation of a bond between two non-adjacent atoms r, s of the polyene as being the perturbation. The basic zero-order wave functions for the first-order perturbation for a doubly degenerate level are then given by :

$$\begin{aligned} \Phi &= C_1\Psi\,(\sin) + C_2\Psi\,(\cos) \\ &= C_1 \sum_{x=1}^{n} A \sin\,[(n\pi x/k) + \varepsilon] + C_2 \sum_{x=1}^{n} A \cos\,[(n\pi x/k) + \varepsilon] \quad . \; . \; . \quad (3) \end{aligned}$$

The first-order perturbation energies are given by the standard secular equation

$$\begin{vmatrix} (H^1_{11} - E) & H^1_{12} \\ H^1_{12} & (H^1_{22} - E) \end{vmatrix} = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

When the non-diagonal terms of the determinant are made to vanish the roots of the secular equation (4) become simply H^1_{11} and H^1_{22}.

The simplest way to solve equation (4), and simultaneously to determine the phase angle ε is to choose ε in such a way that the off-diagonal elements, H^1_{12}, in the determinant vanish. The roots of the secular equation then become H^1_{11} and H^1_{22}, and the coefficients of the atomic orbitals in the perturbed molecular orbitals become :

$$A \sin\,[(n\pi x/k) + \varepsilon] \text{ and } A \cos\,[n\pi x/k) + \varepsilon]$$

[since if H^1_{12} vanishes, either C_1 or C_2 in equation (3) vanishes]. Equating H^1_{12} to zero and considering the perturbation term, P, of the Hamiltonian to be the introduction of a cross-link between atoms r and s, we have :

$$H^1_{12} \equiv \int \Psi\,(\sin)\, P\Psi\,(\cos)\, d\tau = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\textit{i.e.} \qquad \int \sum_{x=1}^{n} A \sin\,[(n\pi x/k) + \varepsilon] \sum_{x^1=1}^{n} A \cos\,[(n\pi x^1/k) + \varepsilon]\psi_x\,.\,P\psi_{x},\, d\tau = 0 \quad . \; . \quad (6)$$

$$\text{Now} \qquad \int \psi_x P\,.\,\psi_{x^1} d\tau = -\,\beta \text{ when } \begin{aligned} x = r,&\ x^1 = s \\ x^1 = r,&\ x = s \end{aligned} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$
$$= 0 \text{ otherwise}$$

Therefore, from (6), we have :

$$\sum_{c}\{A \sin\,[(n\pi r/k) + \varepsilon]A \cos\,[(n\pi s/k) + \varepsilon] + A \sin\,[(n\pi s/k) + \varepsilon] \cos\,[n\pi r/k + \varepsilon]\} = 0 \;. \quad (8)$$

where the summation is taken over all the cross-links formed in the molecule.

Now, from (8) we see that

$$\sum_{c} \sin\,\{[n\pi(r + s)/k + 2\varepsilon]\} = 0$$

$$\textit{i.e.,} \qquad \sum_{c} \sin\,[n\pi(r + s)/k] \cos 2\varepsilon + \sum_{c} \cos\,[(n\pi(r + s)/k]\,.\, \sin 2\varepsilon = 0$$

$$\text{Therefore,} \qquad \tan 2\varepsilon = -\,\frac{\sum_{c} \sin\,[n\pi(r + s)/k]}{\sum \cos\,[n\pi(r + s)/k]} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

Equation (9) allows a determination of the phase factor and thereby allows simple expressions for the perturbation energies. In practice it is found that the phase factor need be calculated only for molecules having no plane of symmetry; in the other cases it can be made equal to zero by adopting the correct numbering, and this in turn can be found by inspection since the plane of symmetry must be a nodal plane for one member of each pair of degenerate eigenfunctions. The perturbation energies are then given by the equations :

$$E^1\,(\sin) = H^1_{11} = \int \Psi\,(\sin)\,.\,P\,.\,\Psi\,(\sin)\,.\,d\tau \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$E^1\,(\cos) = H^1_{22} = \int \Psi\,(\cos)\,.\,P\,.\,\Psi\,(\cos)\,.\,d\tau \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From (10) :

$$E^1 = \int \sum_{x=1}^{n} \sum_{x^1=1}^{n} A^2\,.\,\sin\,(n\pi x/k)\,.\,\sin\,(n\pi x^1/k)\,.\,\psi_{(x)}\,.\,P\,.\,\psi_{(x^1)}\,.\,d\tau$$

where the phase factor has been embodied in the values x and x^1. When the values given in equations (7) are substituted for the integral equation (10) becomes :

$$\begin{aligned} E^1\,(\sin) &= -\,A^2\beta\{[\sin\,(n\pi r/k)\,.\,\sin\,(n\pi s/k)] + [\sin\,(n\pi s/k)\,.\,\sin(n\pi r/k)]\} \\ &= -\,A^2\beta\{\cos\,[n\pi(r-s)/k] - \cos\,[n\pi(r+s)/k]\} \quad . \quad . \quad . \quad . \quad . \quad (12) \end{aligned}$$

Similarly equation (11) simplifies to

$$E^1\,(\cos) = -\,A^2\beta\{\cos\,[n\pi(r-s)/k] + \cos\,[n\pi(r+s)/k]\} \quad . \quad . \quad . \quad (13)$$

When more than one cross-link is being formed the values are given by

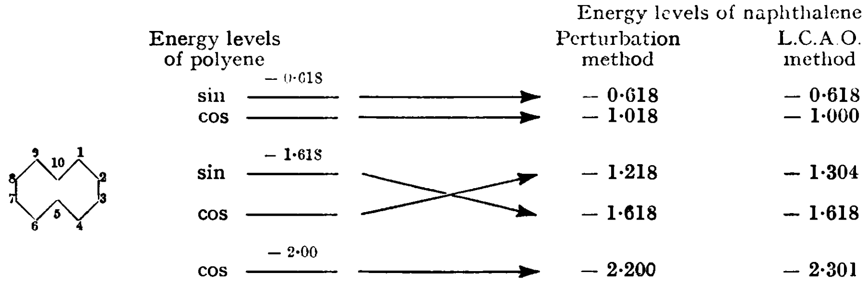
$$E^1\sin\,(\cos) = -\sum_{\text{cross links}} A^2\beta\ \{\cos\,[n\pi(r-s)/k]\,(\mp)\,\cos\,[n\pi(r+s)/k] \quad . \quad . \quad (14)$$

since first-order perturbations are additive.

Equations (14) now allow the determination of the change in energy of the orbitals of the cyclic polyene when cross-links are found to give the polycyclic compound.

The Figure illustrates how the method is used in the determination of the energy levels of naphthalene. The parent cyclic polyene is shown on the left; the cross-link is to be introduced between atoms 5 and 10, and the numbering of the ring is such as to allow the phase factor to vanish. The orbital energies (overlap being neglected) of the polyene are given in the first column and their new values, after the introduction of the cross-link, are shown in the second column. The third column gives the energy levels calculated by the usual L.C.A.O. procedure.

Energy levels of naphthalene, overlap being neglected.



Similar calculations have been performed on sixteen polycyclic aromatic hydrocarbons, with the results given in Table 1, together with the corresponding values calculated by the usual L.C.A.O. method. Also given are the resonance energies and the four lowest electronic transition energies involved in light adsorption, together with a comparison of these values (both readily obtained from a knowledge of the orbital energies) with those obtained by the L.C.A.O. method.

Bond Orders.—By considering a polycyclic hydrocarbon as formed from a completely conjugated cyclic polyene by the introduction of cross-links, it is also possible to obtain a value of the bond orders of the polycyclic hydrocarbons in a simple manner. We make use of an expression, first introduced by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **191**, 39) and applicable to conjugated systems, termed the bond-bond polarizability. This value is defined * by :

$$\pi mn,\ tu = \frac{\partial p_{mn}}{\partial \beta_{tu}} = -\,2\sum_r \sum_s \frac{(a_{mr}a_{ns} + a_{ms}a_{nr})(a_{tr}a_{us} + a_{ts}a_{ur})}{(\varepsilon_r - \varepsilon_j)} \quad . \quad . \quad . \quad (15)$$

* The negative sign in equation (15) arises because we have retained the original convention for the signs of energies.

TABLE 1. *Resonance energies, transition energies, and occupied molecular orbital energies of polycyclic hydrocarbons.*

Except for the resonance energies, where it has been neglected, a value of 0·25 has been taken for the overlap integral. The values are all in terms of γ, the appropriate unit when overlap is included. The L.C.A.O. values have been taken from data given by Pullman and Pullman, " Les Theories Electroniques de la Chimie Organique," Masson, Paris, 1952.

	Resonance energy		Electronic transitions		Orbital energies	
Compound	Perturbation method	L.C.A.O.	Perturbation method	L.C.A.O.	Perturbation method	L.C.A.O.
Naphthalene	3·344	3·683	1·266	1·266	0·535	0·535
			1·542	1·531	0·811	0·800
			1·902	1·869	0·934	0·983
			2·178	2·133	1·155	1·152
					1·419	1·461
Anthracene	4·622	5·314	0·847	0·837	0·379	0·375
			1·202	1·262	0·734	0·800
			1·539	1·709	0·794	0·800
			1·894	2·133	1·004	1·045
					1·075	1·045
					1·292	1·333
					1·455	1·506
Phenanthrene	4·618	5·448	1·314	1·239	0·552	0·526
			1·406	1·358	0·644	0·645
			1·501	1·478	0·804	0·889
			1·593	1·597	1·016	0·984
					1·018	1·100
					1·279	1·311
					1·455	1·514
Naphthacene	5·843	6·932	0·596	0·594	0·276	0·275
			0·892	0·970	0·572	0·651
			1·077	1·240	0·776	0·800
			1·373	1·616	0·863	0·919
					1·000	0·978
					1·035	1·073
					1·226	1·231
					1·361	1·417
					1·474	1·526
3 : 4-Benzophenanthrene	5·842	7·187	1·085	1·159	0·470	0·497
			1·230	1·230	0·615	0·568
			1·359	1·290	0·800	0·800
			1·504	1·361	0·800	0·877
					0·972	1·045
					1·064	1·045
					1·134	1·227
					1·339	1·392
					1·474	1·541
Triphenylene	5·904	7·275	1·233	1·409	0·524	0·584
			1·233	1·409	0·524	0·584
			1·233	1·409	0·690	0·721
			1·233	1·409	0·934	0·973
					0·934	0·973
					1·091	1·008
					1·252	1·320
					1·252	1·320
					1·474	1·551
Chrysene	5·840	7·190	1·027	1·058	0·449	0·460
			1·211	1·259	0·633	0·661
			1·375	1·448	0·672	0·718
			1·559	1·649	0·905	0·933
					0·923	0·973
					1·045	1·112
					1·193	1·193
					1·353	1·405
					1·474	1·538

TABLE 1. (*Continued.*)

	Resonance energy		Electronic transition		Orbital energies	
Compound	Perturbation method	L.C.A.O.	Perturbation method	L.C.A.O.	Perturbation method	L.C.A.O.
1 : 2-Benzanthracene	5·840	7·101	1·027	0·916	0·449	0·406
			1·211	1·117	0·633	0·607
			1·375	1·277	0·672	0·800
			1·559	1·477	0·905	0·903
					0·923	0·994
					1·045	1·084
					1·193	1·220
					1·353	1·409
					1·474	1·533
Pentacene	7·068	8·544	0·433	0·441	0·205	0·208
			0·676	0·768	0·448	0·535
			0·782	0·939	0·732	0·800
			1·025	1·266	0·763	0·800
					0·936	0·935
					0·942	0·983
					1·053	1·089
					1·154	1·152
					1·311	1·333
					1·409	1·461
					1·486	1·537
1 : 2-3 : 4-Dibenzanthracene	7·124	8·942	0·989	1·014	0·434	0·444
			1·088	1·176	0·533	0·606
			1·158	1·312	0·570	0·660
			1·257	1·475	0·769	0·859
					1·000	0·924
					1·065	0·991
					1·073	1·026
					1·073	1·204
					1·205	1·320
					1·350	1·428
					1·486	1·561
1 : 2-7 : 8-Dibenzanthracene	7·068	8·879	1·167	0·999	0·500	0·438
			1·179	1·096	0·512	0·535
			1·188	1·169	0·670	0·717
			1·200	1·266	0·755	0·800
					0·860	0·953
					0·997	0·983
					1·042	1·097
					1·069	1·152
					1·261	1·307
					1·389	1·461
					1·486	1·547
Picene	7·072	8·943	1·074	1·020	0·466	0·446
			1·154	1·155	0·546	0·581
			1·217	1·266	0·607	0·708
			1·297	1·401	0·814	0·800
					0·814	0·924
					0·970	1·018
					1·061	1·109
					1·089	1·123
					1·283	1·305
					1·394	1·459
					1·486	1·552
Pentaphene	7·072	8·763	1·074	0·885	0·466	0·394
			1·154	0·952	0·546	0·461
			1·217	0·993	0·607	0·800
			1·297	1·060	0·814	0·800
					0·814	0·944
					0·970	0·975
					1·061	1·093
					1·089	1·141
					1·283	1·333
					1·394	1·454
					1·486	1·544

TABLE 1. (*Continued.*)

	Resonance energy		Electronic transitions		Orbital energies	
Compound	Perturbation method	L.C.A.O.	Perturbation method	L.C.A.O.	Perturbation method	L.C.A.O.
1 : 2-5 : 6-Dibenzanthracene ...	7·072	8·880	1·074	1·016	0·466	0·443
			1·154	1·157	0·546	0·584
			1·216	1·269	0·607	0·657
			1·297	1·410	0·814	0·844
					0·814	0·913
					0·970	1·045
					1·061	1·045
					1·089	1·173
					1·283	1·301
					1·394	1·463
					1·486	1·547
Azulene	2·954	3·364	0·973	0·968	0·428	0·426
			1·266	1·268	0·721	0·726
			1·556	1·566	0·956	1·013
			1·849	1·866	1·171	1·169
					1·419	1·465
Pentalene	2·156	2·456	—	—	0·444	0·421
					0·745	0·800
					1·045	1·045
					1·440	1·478

where ∂p_{mn} is the change in bond order of the bond mn following a change in the resonance integral $\partial\beta_{tu}$ between atoms t and u; a_{mr}, a_{ns}, etc., are the coefficients of the atomic orbitals of atoms m, n, etc., in the rth and sth molecular orbitals respectively; and r and s refer in turn to the bonding and antibonding orbitals and have energy values of ε_r and ε_s respectively.

In the case of cyclic polyenes, where the energy levels are doubly degenerate, equation (15) can be shown to be also valid if the correct zero-order molecular orbitals given in the previous section are used as a basis in its derivation. It follows then that the change in bond order of the bond between atoms m and n in a cyclic polyene, caused by the introduction of a cross link between atoms t and u, is given by :

$$\partial p_{mn} = -2\beta \sum_r \sum_s \frac{(a_{mr}a_{ns} + a_{ms}a_{nr})(a_{tr}a_{us} + a_{ur}a_{ts})}{\varepsilon_r - \varepsilon_s} \quad . \quad . \quad . \quad . \quad (16)$$

This expression can be applied in the present calculations by using the values for the coefficient given in equation (1). Since each level is degenerate, we have

$$a_{mr} = \cos\,[(m\pi r/k) + \varepsilon]\,;\; a^1{}_{mr} = \sin\,[(m\pi r/k) + \varepsilon]$$

these being the coefficients in the two distinct molecular orbitals ψm (cos) and ψm (sin) of common energy E_m.

If the alternate atoms of the cyclic polyene are starred, then, by using the fact that the coefficients of the atomic orbitals of starred atoms in the bonding molecular orbitals of alternate hydrocarbons are equal in magnitude and sign to the same coefficients in the corresponding antibonding orbitals whereas for unstarred atoms the two coefficients are of equal magnitude but differ in sign, equation (16) can be readily simplified to the form :

$$\begin{aligned}\partial p_{mn} = {} & \frac{1}{k^2(1 - \cos s\pi/k)} \cdot \sum_{s \neq k} \left[\cos\frac{s\pi(m-u)}{k} + \cos\frac{s\pi(n-t)}{k} + \cos\frac{s\pi(m-t)}{k} + \cos\frac{s\pi(n-u)}{k}\right] \\ & + \frac{1}{k^2\left(\cos\frac{r\pi}{k} - \cos\frac{s\pi}{k}\right)} \sum_{r \neq 0} \sum_{s \neq k} \left[\cos\frac{r\pi(m-t)}{k} \cdot \cos\frac{s\pi(n-u)}{k} + \cos\frac{r\pi(m-u)}{k} \cos\frac{s\pi(n-t)}{k}\right. \\ & \left. + \cos\frac{r\pi(n-t)}{k} \cdot \cos\frac{s\pi(m-u)}{k} + \cos\frac{r\pi(n-u)}{k} \cdot \cos\frac{s\pi(m-t)}{k}\right] \quad . \quad . \quad (17)\end{aligned}$$

The first square bracket of this expression results from the combinations $r \neq 0$, $s = k$, and $r = 0$, $s \neq k$; and the second from $r \neq 0$, $s \neq k$; the value of the perturbation for the combination $r = 0$, $s = k$ vanishes. As before, if more than one cross-link is formed the perturbations are additive.

The bond orders of polycyclic hydrocarbons are then found by adding the perturbation values given by equation (17) to the bond order of any bond in the unperturbed cyclic polyene; the bonds of the unperturbed polyene all have the same bond order which is given by :

$$p_{mn} = 2\sum_{r} A^2 \cos (\pi r/k) \text{ where } \left. \begin{aligned} A^2 &= 1/2k \text{ for } r = 0 \\ &= 1/k \text{ for } r \neq 0 \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

By this method the bond orders of naphthalene, anthracene, phenanthrene, 1 : 2-benzanthracene, and azulene have been estimated, with results given in Table 2 together with those found by the usual L.C.A.O. method. Also given are the bond lengths predicted by both methods (estimated from the Coulson bond-order–bond-length curve) and a comparison of these values with known experimental bond lengths.

TABLE 2.

		Bond order		Predicted bond length		
Compound	Bond	Perturbation method	L.C.A.O. method	Perturbation method	L.C.A.O. method	Obs. length
Naphthalene ……………	*A*	0·732	0·725	1·38	1·38	1·36
	B	0·584	0·555	1·41	1·41	1·42
	C	0·638	0·603	1·40	1·40	1·395
	D	0·574	0·518	1·41	1·42	1·395
Anthracene ………………	*A*	0·761	0·738	1·37	1·38	1·365
	B	0·565	0·535	1·41	1·42	1·42
	C	0·578	0·586	1·41	1·41	1·39
	D	0·557	0·485	1·41	1·43	1·44
	E	0·602	0·606	1·40	1·40	1·39
Phenanthrene ……………	*A*	0·674	0·590	1·39	1·41	—
	B	0·663	0·702	1·39	1·38	—
	C	0·669	0·623	1·39	1·40	—
	D	0·669	0·705	1·39	1·38	—
	E	0·662	0·575	1·39	1·41	—
	F	0·532	0·506	1·42	1·42	—
	G	0·773	0·775	1·37	1·37	—
	H	0·490	0·461	1·43	1·43	—
	I	0·649	0·542	1·40	1·42	—
1 : 2-Benzanthracene …	*A*	0·719	0·597	1·38	1·41	—
	B	0·635	0·695	1·40	1·38	—
	C	0·713	0·628	1·38	1·40	—
	D	0·637	0·700	1·40	1·38	—
	E	0·703	0·581	1·38	1·41	—
	F	0·492	0·493	1·43	1·43	—
	G	0·800	0·783	1·37	1·37	—
	H	0·503	0·494	1·42	1·43	—
	I	0·703	0·628	1·38	1·40	—
	J	0·572	0·590	1·41	1·41	—
	K	0·631	0·542	1·40	1·42	—
	L	0·709	0·732	1·38	1·38	—
	M	0·636	0·593	1·40	1·41	—
	N	0·706	0·731	1·38	1·38	—
	O	0·632	0·545	1·40	1·42	—
	P	0·560	0·584	1·41	1·41	—
	Q	0·725	0·646	1·38	1·395	—
	R	0·471	0·447	1·43	1·44	—
	S	0·680	0·478	1·39	1·43	—
	T	0·634	0·500	1·40	1·425	—
	U	0·622	0·495	1·40	1·43	—
Azulene …………………	*A*	0·648	0·656	1·395	1·39	—
	B	0·648	0·596	1·395	1·41	—
	C	0·648	0·586	1·395	1·41	—
	D	0·648	0·664	1·395	1·39	—
	E	0·648	0·639	1·395	1·40	—
	F	0·420	0·401	1·44	1·45	—

DISCUSSION

Although the resonance energies, calculated by each of the two methods show considerable discrepancies, yet if one set of values is plotted against the other it is seen that $A = 1{\cdot}35B - 0{\cdot}70$, where A and B are the resonance energies determined by the L.C.A.O. method and the perturbation method respectively. For the acene series of hydrocarbons the resonance energies are consistently lower than for the corresponding " branched " isomers and in these cases the relation $A = 1{\cdot}28B - 0{\cdot}56$ is better. The values given by these equations for the resonance energies are shown in Table 3: the very small percentage errors indicate that the simple perturbation method allows an accurate estimate of the L.C.A.O. resonance energies of alternant polycyclic hydrocarbons.

TABLE 3. *L.C.A.O. resonance energies predicted by the perturbation method, compared with the accurate values.*

Compound	Predicted	Found	Error (%)	Compound	Predicted	Found	Error (%)
Naphthalene	3·71	3·68	0·8	Pentacene	8·49	8·54	0·6
Anthracene	5·35	5·31	0·7	1 : 2-3 : 4-Dibenzanthracene	8·91	8·94	0·3
Phenanthrene	5·54	5·45	1·7	1 : 2-7 : 8-Dibenzanthracene	8·84	8·88	0·4
Naphthacene	6·92	6·93	0·2	Picene	8·84	8·94	1·1
3 : 4-Benzophenanthrene	7·18	7·19	0·1	Pentaphene	8·84	8·76	0·9
Triphenylene	7·27	7·28	0·1	1 : 2-5 : 6-Dibenzanthracene	8·84	8·88	0·4
Chrysene	7·18	7·19	0·1	Azulene	3·21	3·36	4·4
1 : 2-Benzanthracene ...	7·18	7·10	1·4	Pentalene	2·20	2·46	12

The correspondence of the values of orbital and transition energies given by the two methods is also sufficiently close to allow the simple method to have useful applications.

Discrepancies between the two methods are shown in the bond orders and the corresponding estimated bond length. The bond length D of naphthalene calculated by the perturbation method is in slightly the better agreement with experiment. For anthracene the perturbation method gives a better predicted value for bond A but worse values for B and D. The discrepancy for bond D may however not be as great as indicated, for there is some evidence that the experimental value is less than that given in Table 2 (Ahmed and Cruickshank, *Acta Cryst.*, 1952, **5**, 852). In the alternant hydrocarbons both methods commonly predict the bond possessing greatest chemical reactivity. It is interesting also that the introduction of a cross-link between atoms 1 and 5 in *cyclo*decapentaene has no effect on the bond orders; the bond orders of the external bonds in azulene are therefore all equal, and the same as those for *cyclo*decapentaene. It can be shown that this is a general result when a cross-link is introduced between two atoms of like parity, *i.e.*, both starred or unstarred, in a cyclic polyene. Another interesting feature of the perturbation method is that it predicts that all the external bonds of the outer rings in phenanthrene have the same lengths, as do those of benzene; there are also differences predicted by the two methods for 1 : 2-benzanthracene, and comparison with experimental values would be desirable.

So far the only compounds that have been treated by the above perturbation procedure are polycyclic aromatic hydrocarbons having no carbon atom common to more than two rings. It is hoped to extend the method to the more highly condensed systems and also to heterocyclic molecules.

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