SCF-π-Electron Calculations Using Orthogonalised Atomic Orbitals

II. The Incorporation of Variable Bond Order and Variable Electronegativity Refinements

KEITH D. WARREN

Department of Chemistry, University College, Cardiff, Wales

JOHN R. YANDLE*

School of Chemistry, The University, Bristol, England

Modifications of the SCF-LCAO-π-MO method analysed in the previous paper are described in which provision is made for the incorporation of Variable Bond Order and Variable Electronegativity procedures. A comparison is made with the results of other π-electron calculations and values are reported for twenty hydrocarbon systems.

Änderungen der SCF-LCAO-π-MO-Methode aus Teil I werden beschrieben und VBO und VE berücksichtigt. Vergleiche mit anderen π-Elektronenrechnungen werden angestellt. Die Werte für 20 Kohlenwasserstoffe werden mitgeteilt.

Description de modifications de la méthode SCF-LCAO-MO analysée dans l'article précédent, avec introduction des procédés à indices de liaison et électronégativités variables. Comparaison avec les résultats d'autres calculs sur les électrons π; publication de données concernant vingt hydrocarbures.

Introduction

In the previous paper [1] an analysis was made of the Adams-Miller SCF π-electron method [2], in which an orthogonalised basis set of atomic orbitals is used. Despite certain theoretical shortcomings, the method is reasonably satisfactory for the calculation of both ionisation potentials *and* singlet state excitation energies. In its present form however the method requires a knowledge of the geometry of the given system and also takes no explicit account of non-uniform charge distribution. We have therefore modified the standard method to include a Variable Bond Order procedure, to tackle situations in which the molecular geometry is unknown, and a Variable Electronegativity routine, appropriate, for example, for non-alternant systems. We present the results of such calculations on twenty typical hydrocarbons and compare them with those using the standard method, with other calculations, and with the experimental values.

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* Present address: Department of Computer Services, The University, Birmingham, England.

Modification of Method and Results

1. Procedure

Adams and Miller applied their original method only to a limited range of compounds - naphthalene, anthracene, phenanthrene, and the first ten linear polyenes. The encouraging results for these systems suggested a more searching test of the method by applying it to further benzenoid polycyclics, and also to styrene and trans-stilbene, to non-alternant hydrocarbons such as fluoranthene and azulene, and to pseudo-aromatics of the fulvene type. Unfortunately the published method requires knowledge of the geometry of the systems, which in many of our selected cases is not available, whereas in others strong bond alternation occurs, making even the choice of a good approximation difficult.

Initially therefore we used two test molecules – naphthalene and azulene – to develop modifications of the basic procedure. We compared the results using the known structures with those obtained assuming a regular geometry, and as expected, for naphthalene there is very little change. For azulene though, the latter results are significantly poorer because we are using much too short a distance for the 9–10 bond. We therefore introduced a variable bond order (VBO) modification in which the nearest-neighbour r_{pq} distances are recalculated after each iteration using the mobile bond order from the previous cycle, all quantities which depend on these distances ($S_{pq}, (pp/qq)$) also being recalculated each cycle. The results (Table 1) compare very favourably with those obtained using the known fixed geometry. The final figures for the nearest-neighbour bond lengths also agree satisfactorily with the experimental values (Table 5).

Table 1. *Comparative survey of results for naphthalene and azulene*

Singlet excitation energies

Transition symmetry	Method 1[a]		Method 2[a]		Method 3[a]		Bloor, Gilson and Brearley		Experiment	
	(kK.)	f	(kK.)	f	(kK.)	f	(kK.)	f	(kK.)	f
Naphthalene D_{2h}									[b]	
$^1B_{3u}(x)$	34.07	0.004	33.92	0.003	33.81	0.002	32.45	0	32.03	0.002 (x)
$^1B_{2u}(y)$	36.53	0.276	36.74	0.268	36.60	0.267	36.43	0.204	36.39	0.180 (y)
$^1B_{3u}(x)$	47.10	1.951	46.99	1.965	46.80	1.958	45.69	1.949	45.42	1.700 (x)
$^1B_{2u}(y)$	53.04	0.541	52.66	0.576	52.45	0.574	49.63	0.615	52.52	0.210
Azulene C_{2v}									[c]	
$^1B_1(x)$	16.98	0.026	16.38	0.025	15.11	0.025	15.80	0.024	15.80	0.045
$^1A_1(z)$	28.80	0.032	28.59	0.020	27.88	0.023	27.60	0.006	29.50	0.080
$^1B_1(x)$	36.50	0.165	36.36	0.144	36.25	0.132	34.55	0.115	36.10	sh
$^1A_1(z)$	39.23	1.889	38.95	1.872	38.67	1.901	37.64	1.819	36.47	1.100
$^1B_1(x)$	47.60	0.287	47.48	0.329	47.31	0.339	44.99	0.421	42.30	0.380

[a] Method 1: Fixed geometry (exact structure, from crystallographic data, references in Table 5), Method 2: VBO, Method 3: VBO and VE.

[b] Jaffé, H. H., and M. Orchin: Theory and Application of Ultraviolet Spectroscopy. New York: John Wiley and Sons 1962.

[c] Plattner, P. A., and E. Heilbronner: Helv. chim. Acta 30, 910 (1947); 31, 804 (1948).

Since the original method was applied only to alternant hydrocarbons, we also studied the use of a variable electronegativity (VE) refinement, similar to that of Brown and Heffernan [3], to test the method further for non-alternant systems. Because of the arbitrary Z_C value of 2.81 which is used [2], we had difficulty in fixing our parameters for the variation of I_p with Z_p and of Z_p with P_{pp}. The suggested figures are therefore somewhat tentative, and the changes produced by our VE procedure merely indicative of what could be acheived with a more satisfactory set of VE parameters.

For naphthalene there is very little charge separation and the use of the VE procedure, as well as the VBO, makes little difference. For azulene however there is a small but significant effect: the charge distribution becomes more uniform, and the lower spectral energies are slightly reduced, although the results are still very similar to the fixed geometry values (Table 1).

The results for naphthalene are virtually identical to those of Adams and Miller and in good agreement with experiment. For azulene the I.P. agrees well with the experimental figure as do the lower singlet excitation energies. For both molecules the oscillator strengths (which were not given by Adams and Miller) are in good agreement with experiment.

The results for the test molecules were thus sufficiently good to proceed to other systems. We now report results for non-alternant hydrocarbons using (a) the VBO modification and (b) both the VBO and VE modifications, whilst for alternant systems we give only the results using both refinements (although here of course VE has little effect). For all the eighteen further molecules we assumed initially (i) regular geometries for cyclic structures and (ii) for polyenes and exocyclic bonds, long bonds = 1.45 Å, short bonds = 1.35 Å, and bond angles = 120°. The results are shown in Tables 2, 3, 4 and 5.

VBO *Modification:* The nearest neighbour distances were adjusted each cycle using the relationship [4] $r_{pq} = 1.517 - 0.18\,P_{pq}$. Our results appear to indicate that there is no substantial error in assuming this equation to hold for mobile bond orders based on orthogonalised basis sets as well as those derived from localised orbitals.

VE *Modification:* Following Brown and Heffernan [3] we assume that I_p can be expressed as a quadratic function of Z_p. Since to do this we must make an appropriate interpolation using I values for N^+ and O^{++}, there are two problems: (i) to find the value of $(NN/NN)^+$ and $(OO/OO)^{++}$ for trigonal valence states, and (ii) with $Z_C = 2.81$, to assign reasonable values to Z_{N^+} and $Z_{O^{++}}$. Using ground state energies from Moore's table [5] and trigonal valence state energies from Hinze and Jaffé [6], we readily find [taking $I_p - A_p = (pp/pp)$] $(CC/CC) = 11.13$, $(NN/NN)^+ = 16.764$, and $(OO/OO)^{++} = 22.148$ eV. Failing a more adequate relationship, we assume with Paolini [7] that $(pp/pp) = Z_p \times$ const., whence constant = 11.13/2.81 = 3.9609. Thus $Z_{N^+} = 4.232$ and $Z_{O^{++}} = 5.592$. Interpolation [3] now yields,

$$I_p(C) = 0.3238\,Z_p^2 + 6.0302\,Z_p - 8.3411\ .$$

The screening effect of the π-electron density is assumed to follow Slater's rules i.e. $Z_p = 3.16 - 0.35\,P_{pp}$, and the one-centre integral to vary according to the expression $(pp/pp) = 3.9609\,Z_p$.

Table 2. *Comparison of results for alternant hydrocarbons*
Singlet excitation energies

Transition symmetry	Method 3		Bloor, Gilson and Brearley		Experiment	
	(kK.)	f	(kK.)	f	(kK.)	f
Anthracene D_{2h}					a, b	
$^1B_{2u}(y)$	29.04	0.363	28.86	0.274	27.40	0.100
$^1B_{3u}(x)$	41.52	2.773	40.07	2.745	42.27	1.560
$^1B_{2u}(y)$	49.76	0.002	47.61	0.087	45.20	0.210
$^1B_{2u}(y)$	51.39	0.487			54.00	0.410
Phenanthrene C_{2v}					a, c	
$^1A_1(z)$	32.44	0	30.21	0	30.25	0.003 (z)
$^1B_1(x)$	35.35	0.435	34.56	0.311	34.13	0.180 (x)
$^1B_1(x)$	42.31	1.470	40.60	1.541	39.62	1.090
$^1A_1(z)$	42.69	0.819	41.31	0.572		
$^1A_1(z)$	47.42	0.389	45.77	0.303	47.04	0.600
$^1B_1(x)$	51.23	0.225	49.58	0.263		
$^1B_1(x)$	52.16	0.314				
$^1A_1(z)$	53.74	0.002			53.40	0.590
$^1A_1(z)$	56.93	0.373			56.40	0.290
Tetracene D_{2h}					a	
$^1B_{2u}(y)$	24.83	0.509	23.80	0.293	23.80	
$^1B_{3u}(x)$	29.96	0.017	26.57	0		
$^1B_{3u}(x)$	37.91	3.186	36.00	3.331	36.00	
$^1B_{2u}(y)$	40.87	0.130	39.10	0		
$^1B_{2u}(y)$	41.10	0.016	39.44	0.050		
Chrysene C_{2h}					c	
$^1B_u(x, y)$	31.84	0.003			27.50	0.005
$^1B_u(x, y)$	32.34	0.631			30.20	0.360
$^1B_u(x, y)$	40.39	2.214			37.20	1.290
$^1B_u(x, y)$	43.66	1.014			41.38	0.400
$^1B_u(x, y)$	50.17	0.172			51.30	0.220
Perylene D_{2h}					d, e	
$^1B_{3u}(x)$	25.53	1.130	25.12	0.882	23.05	0.330
$^1B_{2u}(y)$	32.94	0.001	29.57	0	39.60	
$^1B_{2u}(y)$	42.32	2.204	40.86	1.631	40.86	0.440
$^1B_{3u}(x)$	52.26	0.750	47.47	0.928	48.50	2.170
Pyrene D_{2h}					a	
$^1B_{3u}(x)$	30.12	0.833	29.72	0.701	29.84	0.470
$^1B_{2u}(y)$	30.21	0.001	27.99	0	26.94	0.002
$^1B_{2u}(y)$	40.15	1.064	39.03	0.956	36.70	0.470
$^1B_{3u}(x)$	45.52	1.507	43.36	1.616	41.54	1.000
Biphenylene D_{2h}					f, g, h	
$^1B_{1g}$(forb.)	24.43	0	26.71	0	25.47	$(\varepsilon_{max} = 250)$
$^1B_{3u}(x)$	31.31	0.001	32.01	0	28.20	$(\varepsilon_{max} = 10^4)$
$^1B_{3u}(x)$	42.36	2.243	41.40	2.015	40.25	$(\varepsilon_{max} = 10^5)$
Trans-butadiene C_{2h}					a	
$^1B_u(x, y)$	42.83	1.031	44.86	0.984	46.05	0.470

Table 2 (continued)

Transition symmetry	Method 3		Bloor, Gilson and Brearley		Experiment	
	(kK.)	f	(kK.)	f	(kK.)	f
Trans-hexatriene C_{2h}					a	
$^1B_u(x, y)$	34.46	1.488	36.37	1.365	36.14	
Trans-stilbene C_{2h}					a	
$^1B_u(x, y)$	32.36	1.355	32.85	1.192	34.01	
$^1B_u(x, y)$	47.21	0.850	46.59	0.784	44.84	
$^1B_u(x, y)$	52.90	0.948	51.57	1.089	49.75	
Styrene C_s					a	
$^1A'(x, y)$	37.07	0	35.75	0	34.97	
$^1A'(x, y)$	40.48	0.726	40.09	0.641	40.82	
$^1A'(x, y)$	49.70	0.470	48.86	0.449		
$^1A'(x, y)$	52.50	0.606	50.87	0.649		

[a] Jaffé, H. H., and M. Orchin: Theory and Applications of Ultraviolet Spectroscopy. New York: John Wiley and Sons 1962. — Friedel, R. A., and M. Orchin: Ultraviolet Spectra of Aromatic Compounds. New York: John Wiley and Sons 1951.
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[e] Tanaka, J.: Bull. chem. Soc. Japan 36, 1237 (1963).
[f] Hochstrasser, R. M.: Canad. J. Chem. 39, 765 (1961).
[g] Hochstrasser, R. M.: J. chem. Physics 33, 950 (1960).
[h] Carr, E. P., L. W. Pickett, and D. Voris: J. Amer. chem. Soc. 63, 3230 (1941).

When the VE treatment is applied all the carbon atoms may no longer be equivalent and different H^0_{pp} and H^0_{pq} quantities need to be defined. Now $H^0_{pp} = E_p - \sum_{r \neq p} (U^0_r : pp)$ and assuming that $\sum_{r \neq p} (U^0_r : pp)$ varies little with charge distribution, we can now correct H^0_{pp} according to the calculated I_p value. E.g. if $I_p < I$ (standard) $= 11.16$ eV, then E_p is less negative i.e. H^0_{pp} is more positive. Thus $(I \text{(standard)} - I_p)$ is added to H^0_{pp} (standard), making it more positive. In addition,

$$H^0_{pq} = \tfrac{1}{2} S_{pq}(E_p + E_q) - \tfrac{1}{2} \left\{ \sum_{r \neq p} (U^0_r : pq) + \sum_{r \neq q} (U^0_r : pq) \right\}$$

and here H^0_{pq} is similarly corrected according to the change in $\tfrac{1}{2} S_{pq}(E_p + E_q)$.

Configuration Interaction: We have throughout imposed a much greater measure of C.I. than in the original treatment. For all systems at least the three highest occupied and the three lowest unoccupied M.O.'s are involved, and in most cases all transitions are included for which the expectation value is 8.0 eV or less. Singly excited states only are included.

Oscillator Strengths: For ease of calculation these have been evaluated using the simple expressions of Mulliken and Rieke [8], and assuming them to apply when an orthogonalised basis set is used. This has though been shown by Peacock [9] to be fully justified since very little change in the calculated values results when f is worked out rigorously.

Table 3. *Comparison of results for non-alternant hydrocarbons*
Singlet excitation energies

Transition symmetry	Method 2		Method 3		Bloor, Gilson and Brearley		Experiment	
	(kK.)	f	(kK.)	f	(kK.)	f	(kK.)	f
Fluoranthene C_{2v}							a, b	
$^1B_1(x)$			28.47	0.019			27.86 ($\log \varepsilon = 3.97$)	
							29.28 (3.91)	
$^1A_1(z)$			30.21	0.576			30.92 (3.79)	
$^1B_1(x)$			33.68	0.078			32.43 (3.61)	
							34.82 (4.76)	
$^1A_1(z)$			39.61	0.465			36.17 (4.46)	
							38.26 (4.24)	
$^1B_1(x)$			43.27	0.091				
$^1A_1(z)$			44.67	0.422			42.43 (4.77)	
$^1A_1(z)$			44.93	0.341				
$^1B_1(x)$			45.44	1.207			45.87 (5.0)	
$^1A_1(z)$			49.78	0.752				
Acenaphthylene C_{2v}							c	
$^1B_1(x)$	23.86	0.044	23.30	0.040	24.66	0.019	24.27 ($\log \varepsilon = 2.19$)	
$^1A_1(z)$	31.81	0.345	31.73	0.339	30.57	0.155	30.03 (3.69)	
$^1B_1(x)$	32.51	0.205	32.41	0.209	31.22	0.275	31.05 (4.01)	
$^1A_1(z)$	40.43	0	40.16	0.004	38.86	0	37.73 (3.48)	
$^1B_1(x)$	46.65	1.123	46.56	1.101	44.14	1.296	43.48 (4.72)	
Fulvene C_{2v}							d, e	
$^1B_1(x)$	22.52	0.034	21.40	0.029	24.57	0.034	27.60	0.012
$^1A_1(z)$	38.33	0.577	38.37	0.561	39.10	0.631	41.30	0.320
Fulvalene D_{2h}							e	
$^1B_{2u}(y)$	16.35	0.025	15.24	0.021	17.50	0.030	? Tail	
$^1B_{3u}(x)$	28.92	1.187	29.07	1.161	29.71	1.201	24.00	w
							31.90	0.400
$^1B_{3u}(x)$	50.08	0.341	50.11	0.395				
Heptafulvene C_{2v}							f	
$^1B_1(x)$	18.60	0.046	17.97	0.043	21.58	0.040	23.45 ($\log \varepsilon = 2.50$)	
$^1A_1(z)$	32.65	0.467	32.55	0.466	32.93	0.440	35.85 (4.00)	
$^1B_1(x)$	46.56	0.238	46.32	0.233	46.55	0.095	47.00 (4.80)	
$^1A_1(z)$	48.38	1.586	48.13	1.589	47.32	1.297		
Heptafulvalene D_{2h}							e	
$^1B_{2u}(y)$	11.59	0.025	10.96	0.022	15.42	0.013	? Tail	
$^1B_{3u}(x)$	23.23	1.368	23.28	1.356	23.85	1.285	27.60	0.380
$^1B_{2u}(y)$	42.30	0.335	42.06	0.330	41.87	0.279		
Sesquifulvalene C_{2v}							e	
$^1B_1(x)$	17.68	0.025	17.07	0.023	19.96	0.010		
$^1B_1(x)$	20.31	0.027	19.22	0.026	20.58	0.029		
$^1A_1(z)$	24.11	1.104	24.20	1.128	24.24	1.087	24.80	0.470
$^1A_1(z)$	40.59	0.215	40.39	0.240	39.50	0.312		

[a] Maddams, N. F., and R. Schnurmann: J. chem. Physics **19**, 973 (1951).
[b] Orchin, M., and L. Reggel: J. Amer. chem. Soc. **69**, 505 (1947).
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Table 4. *Comparison of calculated and experimental ionisation potentials*

Molecule	I. P. Calculated (Method 3)	I. P. Experimental		
Naphthalene	8.35	8.26[a]	8.12[e]	8.46[f]
Anthracene	7.66	7.55[a]	7.85[f]	
Phenanthrene	8.23	8.03[a]	8.11[g]	
Tetracene	7.22	7.00[b]		
Chrysene	7.90	7.80[b]	7.71[g]	
Perylene	7.33	7.15[b]	7.13[g]	
Pyrene	7.64	7.55[b]		
Biphenylene	7.90	—		
Trans-butadiene	9.29	9.07[c]		
Trans-hexatriene	8.53	8.23[c]		
Trans-stilbene	8.01	7.95[b]		
Styrene	8.72	8.55[b]		
Azulene	7.47	7.72[d]	7.50[h]	
Fluoranthene	8.14	—		
Acenaphthylene	8.24	—		
Fulvene	8.54	—		
Fulvalene	8.69	—		
Heptafulvene	7.31	—		
Heptafulvalene	5.96	—		
Sesquifulvalene	7.43	—		

[a] Wacks, M. E., and V. H. Dibeler: J. chem. Physics **31**, 1557 (1959).
[b] Briegleb, G., and J. Czekalla: Z. Elektrochem. **63**, 6 (1959).
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[e] Quoted by Skancke, P. N. in Ref. [18].
[f] McDowell, C. A.: Ind. Chim. Belg. **19**, 713 (1954).
[g] Kuroda, H.: Nature **201**, 1214 (1964).
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Ionisation Potentials: These were determined by the usual application of Koopmans' theorem and are shown in Table 4.

Other Ground State Properties: Work is still in progress concerning the validity of the method for calculating ground state properties, but our early results are less encouraging. For example, in most of the non-alternant hydrocarbons studied, the value of the π-dipole moment is too large by at least a factor of 1.5 to 2.0, and similar results have been reported by Greenshields *et al.* [10].

Excited State Energies: In Tables 2, 3 and 6 we report all the excited singlet state energies corresponding to important transitions up to just over 50 kK. We also list the lowest triplet state energy in each case, but for reasons advanced earlier (see Part I) we attach little or no significance to these latter figures.

Computational Methods: Programs for the basic method and the various modifications were written in ALGOL, and computations carried out on the Bristol University Elliot 503 computer. In most cases the starting vectors for the Fock matrix iteration process were obtained by diagonalisation of the H^λ matrix, but for fluoranthene and the larger alternant hydrocarbons non-convergence ensued, and starting vectors from a simple Pariser-Parr-Pople SCF calculation were used instead. In cases where it was applied, entry to the VE routine was

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Table 5. *Comparison of experimental and calculated bond lengths*
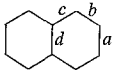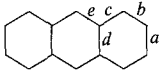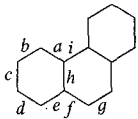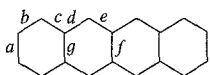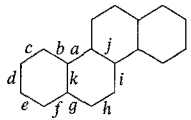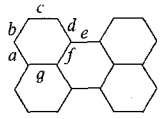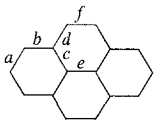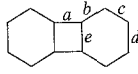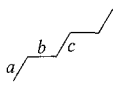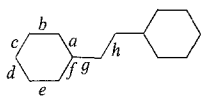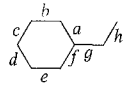
Molecule			R (Expt.) (Å)	R (Calc.) (Å)
Naphthalene[a]		a	1.415	1.413
		b	1.364	1.382
		c	1.421	1.421
		d	1.418	1.417
Anthracene[a]		a	1.419	1.418
		b	1.368	1.378
		c	1.436	1.427
		d	1.428	1.426
		e	1.399	1.407
Phenanthrene[b]		a	1.405	1.412
		b	1.383	1.388
		c	1.398	1.407
		d	1.381	1.388
		e	1.457	1.414
		f	1.390	1.435
		g	1.372	1.370
		h	1.404	1.413
		i	1.448	1.441
Tetracene[c]		a	1.46	1.422
		b	1.38	1.376
		c	1.42	1.431
		d	1.39	1.401
		e	1.40	1.414
		f	1.46	1.431
		g	1.42	1.429
Chrysene[d]		a	1.468	1.436
		b	1.409	1.415
		c	1.381	1.386
		d	1.394	1.409
		e	1.363	1.385
		f	1.428	1.417
		g	1.421	1.430
		h	1.369	1.374
		i	1.428	1.427
		j	1.401	1.404
		k	1.409	1.427
Perylene[e]		a	1.400	1.421
		b	1.370	1.384
		c	1.418	1.410
		d	1.397	1.393
		e	1.471	1.454
		f	1.425	1.424
		g	1.424	1.417
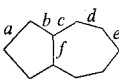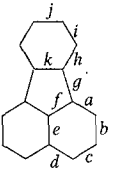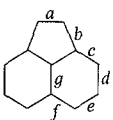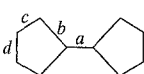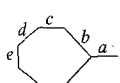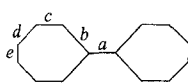
Table 5 (continued)

Molecule		R (Expt.) (Å)	R (Calc.) (Å)
Pyrene[f]	a	1.380	1.396
	b	1.420	1.407
	c	1.417	1.419
	d	1.442	1.437
	e	1.417	1.427
	f	1.320	1.369
Biphenylene[g]	a	1.52	1.476
	b	1.38	1.385
	c	1.42	1.413
	d	1.35	1.385
	e	1.38	1.422
Trans-butadiene[h]	a	1.35	1.349
	b	1.46	1.452
Trans-hexatriene	a		1.351
	b		1.448
	c		1.362
Trans-stilbene[i]	a		1.405
	b		1.396
	c		1.398
		Avge. = 1.39	
	d		1.398
	e		1.395
	f		1.406
	g	1.45	1.452
	h	1.35	1.360
Styrene	a		1.405
	b		1.395
	c		1.398
	d		1.397
	e		1.396
	f		1.404
	g		1.455
	h		1.348

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Table 5 (continued)

Molecule			R (Expt.) (Å)	R (Calc.) (Å)
Azulene[j]		a	1.394	1.399
		b	1.395	1.407
		c	1.391	1.405
		d	1.400	1.400
		e	1.392	1.401
		f	1.498	1.466
Fluoranthene		a		1.389
		b		1.412
		c		1.383
		d		1.423
		e		1.413
		f		1.428
		g		1.456
		h		1.400
		i		1.399
		j		1.397
		k		1.415
Acenaphthylene		a		1.363
		b		1.448
		c		1.392
		d		1.411
		e		1.383
		f		1.423
		g		1.412
		h		1.429
Fulvene		a		1.357
		b		1.459
		c		1.362
		d		1.443
Fulvalene		a		1.378
		b		1.456
		c		1.362
		d		1.448
Heptafulvene		a		1.362
		b		1.454
		c		1.366
		d		1.436
		e		1.371
Heptafulvalene		a		1.388
		b		1.447
		c		1.368
		d		1.439
		e		1.369

[j] Hanson, A. W.: Acta crystallogr. **19**, 19 (1965).

Table 5 (continued)
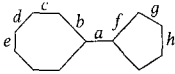
Molecule		R (Expt.) (Å)	R (Calc.) (Å)
Sesquifulvalene	a		1.396
	b		1.440
	c		1.375
	d		1.426
	e		1.378
	f		1.440
	g		1.373
	h		1.430

Table 6. *Comparison of calculated and experimental triplet state energies*

	$^3\Delta E_1$ (Calc.)	$^3\Delta E_1$ (Adams and Miller)	$^3\Delta E_1$ (Expt.)
Naphthalene	2.18	2.71	2.64[a]
Anthracene	1.55	1.94	1.82[a]
Phenanthrene	2.53	3.01	2.68[b,c]
Tetracene	1.07	—	2.43[c]
Chrysene	2.76	—	2.48[b,c]
Perylene	1.84	—	2.08[b,c]
Pyrene	1.77	—	2.08[b,c]
Biphenylene	1.87	—	—
Trans-butadiene	1.05	1.20	3.20[d]
Trans-hexatriene	0.71	1.25	2.60[d]
Trans-stilbene	2.16	—	—
Styrene	1.91	—	—
Azulene	1.42	—	—
Fluoranthene	2.24	—	2.29[b]
Acenaphthylene	1.47	—	—
Fulvene	0.78	—	—
Fulvalene	0.75	—	—
Heptafulvene	0.75	—	—
Heptafulvalene	0.54	—	—
Sesquifulvalene	1.02	—	—

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delayed until a fairly high degree of self-consistency had been attained, since otherwise here also non-convergence could result.

2. Discussion of Results

I. Spectra

The series benzene, ethylene, styrene, stilbene is a crucial one for testing theoretical methods since the basic parameters, defined usually to fit the data for the first two compounds, should necessarily yield good results for styrene and

stilbene. In fact this is so here: our results satisfactorily reproduce the shift of the
p-band in benzene on substitution by a vinyl and by a styryl group, compare
favourably with experiment and with the values given by Bloor et al. [11], and
are certainly superior to those of Fischer-Hjalmars [12] and of Beveridge and
Jaffé [13]. For the polyenes, butadiene and hexatriene, our results are essentially
similar to those of Adams and Miller, but for naphthalene and phenanthrene they
agree considerably better with experiment, due primarily to the greater measure
of C.I. used. For naphthalene the use of the VE and VBO refinements produces
a small improvement over the fixed geometry results and the final figures are
comparable with those given in the survey by Bloor et al. [11]. For anthracene the
results are all slightly too high, and here the use of more extensive C.I. produces
only a marginal improvement over Adams and Miller's values.

For biphenylene the position of the forbidden $^1B_{1_g}$ transition is fairly well
predicted, but the calculated oscillator strength for the $^1B_{3_u}$ transition at 31.31 kK.
is much too low to correspond properly with the observed strong band at 28.20 kK.
The position and intensity of the highest $^1B_{3_u}$ level is though satisfactorily given,
and the figures give as good an overall description of the excited states as is
usually possible for this molecule.

For azulene the overall results reproduce the observed spectrum well, with the
exception of the highest $^1B_1$ level which is ca. 5 kK. too high, and the calculated
intensities are in good agreement with experiment. Otherwise the values compare
well with those of Bloor [11] and of Flurry and Bell, who used non-neighbour
β terms [14] (although these authors claim their results to be superior to those
obtained by the Adams-Miller technique). For fluoranthene our figures compare
satisfactorily with the results of a recent ASMOCI calculation [15], and also
describe adequately the positions and intensities of the observed transitions whilst
for acenaphthylene our results, though not as good as Bloor's, still give a reasonably
good account of the spectrum.

For the non-benzenoid pseudo-aromatic compounds greater disparities
between the observed and calculated spectra are to be expected. In all these
compounds the bands are broad with ill-defined maxima, and the molecules of
this type all exhibit marked bond alternation, as confirmed by our VBO results.
Since relatively small changes in the assumed geometry of molecules of this type
can have appreciable effects on the calculated transition energies, it is clear that
unless the total energy can be minimised with respect to the positions of all the
atoms (and not just nearest-neighbours) calculations on this class of compounds
especially must remain susceptible to the errors inherent in a guessed fixed
geometry or to the inconsistencies in geometry produced by a VBO approach.
It is therefore gratifying that our results adequately reproduce the main features of
the spectra and compare favourably with those of Bloor [11].

It is though apparent that some type of VBO method is needed to give satis-
factory results for the pseudo-aromatics. The early work of Nakajima and Katagiri,
using a method based specifically on bond alternation [16] has since been dis-
counted because of the lack of C.I. but in their ASMOCI work on non-alternant
systems [15] Koutecky, Hochman, and Michl predicted that allowance for bond
alternation would greatly improve the fit between theory and experiment. Conse-

quently, Bloor *et al.* [11] by their variable β method obtained quite significant improvements on Koutecky's results.

It is too early to assess the value of our VE modification, since it is not optimised for the calculation of ground state properties such as dipole moments, which best reflect VE procedures, and until the best value of Z_C is established (see Part I) any VE parameters are quite arbitrary. We therefore merely report without comment the small effects produced by the use of the modification in non-alternant systems.

II. Ionisation Potentials

The calculated and, where available, the experimental values for the twenty compounds are given in Table 4. Where the latter are known, the calculated results are all in excellent agreement, despite the empirical nature of the internal correction used in the Adams-Miller method to compensate for the failure of Koopmans' theorem.

For most of the non-alternant compounds no experimental I.P.'s are known, but it is interesting to note that for the pseudo-aromatics the calculated I.P.'s are generally lower than those for benzenoid systems of a comparable structure (e.g. benzene 9.52 eV, fulvene 8.54 eV) as would be expected from our knowledge of the chemical behaviour of these molecules.

Finally we note that calculations for open-shell compounds would probably require some changes in the H^0_{pp} parameters, since the calculations of Hoyland and Goodman [17] indicate that deviations from Koopmans' theorem do not exhibit the same approximate constancy for radicals as for closed-shell structures.

III. Bond Lengths

The bond lengths obtained with our VBO modification are shown in Table 5 together with the available experimental values as determined by X-ray diffraction. The agreement with experiment is generally very satisfactory, and certainly comparable with that obtained by Skancke [18, 19].

For naphthalene and anthracene the agreement is extremely good, the deviations not exceeding 0.018 and 0.010 Å respectively, but for phenanthrene two of the bonds deviate by about 0.04 Å from the calculated figures. Skancke also observed discrepancies for these particular bonds and suggested that this resulted from deviations from planarity of the molecule due to overcrowding of the H-atoms ortho- to the 13–14 bond. It is though hard to see why these distortions should be confined to the 4–5 and 5–6 bonds since all the other bond lengths are reproduced with considerable accuracy. For chrysene and perylene the agreement with experiment is quite satisfactory, although the long 8–9 bond in chrysene is somewhat underestimated.

For pyrene and biphenylene the crystallographic data are only reliable to ± 0.01 Å but the shorter lengths are somewhat overestimated and the longer bonds underestimated. Such deviations are not unexpected in view of the appreciable steric strain in the systems, but in azulene, in which the other lengths are well reproduced, the long 9–10 bond is also undervalued (by about 0.03 Å).

It seems likely then that this is due to a systematic effect, probably originating in the parameters relating the calculated mobile bond order to the nearest-neighbour r_{pq} distances. Possibly the chosen expression is only valid over a limited range of distances, but we are not currently attempting to improve on this relationship since the results as a whole are quite adequate with the present parameters to indicate the utility of the modification when the exact molecular geometry is unknown.

The results for fluoranthene and acenaphthylene are much as expected, the former showing two long bonds in the five-membered ring and the latter strong bond alternation in the five-membered structure. The pseudo-aromatic compounds also show marked bond alternation, as anticipated, and, using the VBO technique, this result is found whether the starting geometry is regular or alternating. Julg and François [20] also observed this effects, and used the extent of bond alternation as a measure of the system's aromaticity.

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Dr. K. D. Warren
Department of Chemistry
University College of South Wales
and Monmouthshire
Cathays Park
Cardiff, Wales (Great Britain)