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The Electronic Spectra of Unsaturated Hydrocarbons
A VESCF-CI Treatment

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A modified Pariser-Parr method, which allows for the inductive effect of alkyl groups by a VESCF method, has been applied to the calculation of the electronic spectra of a number of hydrocarbons. All singly- and doubly-excited configurations are included in the configuration interaction treatment, except for large molecules for which the configuration interaction matrices are truncated to an order of 110. The red shifts which result from methylation of the polyenes are well calculated. For azulene, the shift to either the red or the blue, depending on the location of the substituent, is also well calculated. The largest deviation between the calculated and experimental transition energies for all of the compounds studied was 1.1 eV, while the standard deviation of all observed transitions for planar compounds was 0.24 eV. The ionization potentials and the singlet-triplet transitions of these compounds were also studied.

Die Spektren einer Reihe von Kohlenwasserstoffen wurden nach einer modifizierten Pariser-Parr-Methode, bei der der induktive Effekt von Alkylgruppen mittels eines VESCF-Verfahrens berücksichtigt wird, berechnet, wobei alle ein- und zweifach angeregten Konfigurationen eingeschlossen wurden außer bei sehr großen Molekülen, wo deren Zahl auf 110 begrenzt wurde. Dabei ergeben sich in schöner Weise die Rotverschiebungen, die bei Methylierung von Polyenen beobachtet werden, desgleichen die Rot- und Violettverschiebungen je nach Ort des Substituenten bei Azulen. Die größten Abweichungen zwischen berechneten und beobachteten Übergangsenergien ist 1,1 eV, die Standardabweichung bei planaren Verbindungen 0,24 eV. Ferner wurden Ionisationspotentiale sowie Sigulett-Triplett-Übergänge der behandelten Verbindungen untersucht.

Une méthode Pariser-Parr modifieé, qui tient compte de l'effet inductif des groupes alkyles dans le cadre VESCF, a été employeé pour calculer les spectres électroniques de quelques hydrocarbures. Toutes les configurations mono- et di-excitées sont comprises dans le traitement d'interaction de configurations, excepté pour les grosses molécules; pour ces dernières, l'ordre des matrices d'interaction de configuration a été réduit à 110. Les déplacements versle rouge, après méthylation de polyènes, sont bien calculés. Pour l'azulène, les déplacements vers le rouge ou le bleu, suivant le lieu de substitution, sont également bien calculés. La plus grande déviation entre les énergies de transition calculée et expérimentale était de 1.1 eV pour tous les produits étudiés, alors que la déviation standard de toutes les transitions observeés était de 0,24 eV dans les composés planaires. Le potential d'ionisation et les transitions singulet-triplet ont aussi été étudiés.

Introduction

In an earlier paper [2], it was shown that the Pariser-Parr method for the prediction of electronic spectra of unsaturated hydrocarbons could be modified by using experimental values for the ionization potentials of small hydrocarbon radicals in constructing the core matrix. The results were encouraging in that the well-known red shifts which are observed experimentally upon alkyl substitution were approximately accounted for. There were a number of obvious refinements in the method that seemed worthwhile, some of which have been made and are noted below. We then considered it desirable to apply this revised method to an expanded number of types of structures, specifically including compounds which are known to exhibit unusual behavior, such as the methylated azulenes. The Pariser-Parr method is now widely used for the calculation of electronic spectra. Perhaps 90% of the molecules previously studied have their spectra calculated to within one electron volt, but his is poor compared to the accuracy with which the experimental measurements can be carried out. With a restricted group of compounds, one can of course do much better than this, but the test of the usefulness of the theory is really measured by how well can be done with compounds where the results are not obviously predictable by inspection. Specifically, one wants to be able to treat large and small hydrocarbons (and ultimately non-hydrocarbons as well), cyclic and acyclic, aromatic and non-aromatic, planar and non-planar, conjugated, unconjugated, and cross-conjugated. When any published method of calculation is applied to such a variety of systems, the results always fall very far short of the accuracy obtainable by experimental measurement, and hence these methods are not satisfactory from a predictive point of view. We have found, for example, that inclusion of doubly-excited configurations in the configuration interaction treatment has very little effect on about 90% of the molecules studied, but it has a substantial effect in certain cases [*2*]. Obviously, then, while the inclusion of these doubly-excited configurations will not make any difference in many cases, one cannot really hope to do an adequate job in the general case unless they are included, or unless some alternative method of accounting for their effect is devised. Properly, of course, one should include *all* configurations. For molecules of the size which are currently of interest to organic chemists, this is quite impossible. On the other hand, it would be very desirable to know at what point the configuration interaction treatment can be terminated without serious consequences in the final results. A few studies along these lines have been reported previously [*2*, *17*]. In the present paper the ground state is considered, along with all singly- and doubly-excited configurations. In subsequent papers triply-excited configurations and truncation of the configuration interaction matrices will be considered in detail.

Method of Calculation

The present method differs from that used previously [*2*] in the following respects:

1. The π system was subjected to a variable electronegativity self-consistent field (VESCF) treatment at the outset, and the resulting SCF orbitals obtained were used for the configuration interaction, instead of using the McWeeny-Peacock orbitals as previously. The latter are merely approximations to the SCF orbitals, and it seems more reasonable to use the actual SCF orbitals as these are now easily available.

2. Penetration effects from carbon atoms were considered. The earlier method accounted for the effect of a hydrogen atom or of a methyl group attached to the carbon atom being considered in terms of the change in orbital exponent and

ionization potential of the core atom brought about by the substituent. This change would be due in part to penetration, and in part to induction. If instead of a substituent, another core atom is attached to the first, then no induction results, but there is still a penetration effect to consider. In the calculation of the spectrum of a molecule such as benzene, inclusion of this penetration effect serves only to change all of the diagonal elements of $\boldsymbol{H}_{\text{core}}$ by an equal amount, and consequently it does not change the calculated spectrum. In a molecule such as naphthalene, the diagonal elements change by different amounts, and so these effects should be included. The values calculated for the ionization potentials of molecules do, of course, depend on whether or not penetration is included. It has often been noted by earlier authors that the results are in better agreement with experiment if penetration is neglected, but this is only the inclusion of an intentional error in an attempt to cancel out an unintentional one, a dangerous procedure at best [*11*].

3. The resonance integrals β are evaluated by an empirical scheme, which differs only slightly from the empirical schemes used earlier. All resonance integrals are included in the calculation. (See Ref. [*9*] for a discussion of the effects of including resonance integrals between non-neighbors). For bound atoms, when S is greater or equal to 0.14, β is taken as proportional to $S/(1 + S)$, as previously*. When S is less than 0.14, which means between non-bound atoms, a polynomial was derived which allows β to fall off somewhat more rapidly than the previous function. Since the function is an empirical one anyway, there seems to be no advantage to the usual type of function, and a better fit to certain of the spectra can be obtained with this revised function. The particular polynomial chosen was

$$44095\,S^5 - 150845\,S^4 + 1785\,S^3 - 80.4\,S^2 + 1.60\,S\,.$$

4. The configuration interaction treatment included all singly- and doubly-excited configurations for both the singlet and triplet states.

5. The ionization potentials of the molecules were calculated with the aid of Koopman's theorem.

Results and Discussion

The calculated and observed singlet and triplet transitions and the ionization energies of the compounds considered are given in Tab. 1. Inspection of the data will show that for the singlet transitions, a great many of the transitions calculated agree to within 0.1 to 0.2 eV with the observed spectra, which is approximately within experimental error of the measurements. For the triplets, not much experimental data are available [*8*], but as was noted in the previous paper, the lowest energy transition can be calculated quite well with only the inclusion of singly-excited configurations in the configuration interaction treatment. When the doubly-excited configurations are included, there is essentially no change. On the other hand, the singly-excited configurations alone did not give very good results for the singlet-triplet transitions of higher energy, but on more intensive scrutiny of the experimental spectra, it is only the (0,0) vibrational transition which can really be determined, since experimental difficulties preclude the observation of the shorter wavelength side of the electronic transition [*6*]; we are, of course, interested in the Franck-Condon band.

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* Except that the proportionality constant was given the numerical value −2.90 eV.

The singlet transitions may be taken up first, as these are the quantities which are best known, and for which the most data and the most reliable data, are available.

We have commented previously that while the Pariser-Parr treatment in its original form always yields oscillator strengths which are too large by a factor of two or three, when the doubly-excited configurations are included in the calculation these quantities are calculated to have smaller values, more in agreement with theoretical predictions of the extinction coefficient — oscillator strength relationship [*12*]. The calculated values still tend to be about 50% too large, however. If we examine first the substituted ethylenes (entries 1—6 in Tab. 1), we note that generally the transition energies calculated are in agreement with the experimental values to within better than 0.3 eV. Since the error in estimating the transition energy from the relatively broad band observed in these spectra is of the order of 0.1—0.2 eV, these numbers are regarded as quite satisfactory.

Next, if we examine the butadiene derivatives (entries 8—20 in Tab. 1), it is found that for the parent butadiene the agreement with experiment is quite satisfactory, as there is predicted a forbidden transition (unobserved) at just slightly longer wavelength than the strong observed transition, which is calculated accurately. There is also predicted a transition at 8.00 eV, which is forbidden and unobserved. For the *cisoid* form of butadiene, as represented by 1,3-cyclohexadiene, the agreement is less good. Even so, the long wavelength transition is predicted to within 0.25 eV of the experimental values. A second transition is predicted at 5.71 eV, with one-tenth the oscillator strength of the long wavelength transition. The latter is actually observed at 6.02 eV, but the observed oscillator strengths are more similar than calculated. An additional transition is predicted at 8.14 eV, with an oscillator strength of 0.62, but no experimental data this far into the ultraviolet have been reported in the literature up until now.

Entry number 22 predicts the singlet transitions for the butadiene molecule when rotated 90°. Non-planar butadienes in more complicated systems where the non-planarity is enforced by outside steric factors are well known compounds, and this is a limit toward which such systems presumably tend. A direct comparison with any experimental data is not, however, possible.

Turning back now to the methylated *s-trans*-butadienes, it may be noted that while the symmetrical ones are analogous to butadiene itself in showing a forbidden and an allowed transition in the range of 5—6 eV, the unsymmetrical dienes (such as 8—12, 15, and 18) are predicted to have both transitions allowed. The oscillator strengths vary considerably, summing for the two transitions to about 0.8 in each case, with an intensity ratio anywhere from about 0 to about 1. In each case the difference in energy between the two transitions which we calculate is of the order of a few tenths of a volt; not enough to expect the two bands to be resolved experimentally. Only one absorption band is observed in each case, so that the experimental value for the energy would in fact be a weighted average for the two transitions. In the table are given the energies of each transition, together with the calculated oscillator strengths. By plotting the predicted bands (with the aid of an automatic plotting program described earlier [*1*]) a single peak with its maximum located between the two transitions was always found. The value given in millimicrons for the calculated spectrum is this average value. Of the compounds for

Table 1

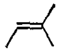
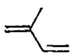
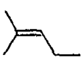
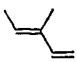
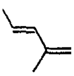
	Singlet Transitions						Triplet Transitions		Ionization Energy		
	Calc.		Obs.				Calc.	Obs.[d]	Calc.	Obs.	
Compound[a]	eV (mμ)	ε[b]	eV (mμ)	ε	Solvent[j]	Ref.	eV	eV	eV	eV	Meth-od[e]
1 	7.35 (169)	17,100	7.28 (170)	17,100		[*14*]	4.19	4.6	12.40 (10.45)[f]	10.52	
2 	7.09 (175)	16,700	7.09 (175)	15,000		[*14*]	4.08		11.85	9.73 9.81	
3 	6.88 (180)	16,300	6.60 (188)	11,300		[*14*]	4.01		11.44	8.95 9.23	
4 	6.86 (181)	16,300	6.85 (178)	13,000		[*14*]	3.92		11.30	9.13 9.24	
5 	6.66 (186)	15,800	6.85 (178)	11,000		[*14*]	3.82		10.88	8.68 8.80	
6 	6.46 (192)	15,400	6.63 (187)	15,600		[*14*]	3.69		10.46	8.30	
7 	5.87 (211) 5.91 (209)	0 34,200	5.92 (209)	25,200		[*3*]	3.14 4.78	3.2	11.19	9.07	
8 	5.77 (215) 5.79 (214)	31,700 1,700	5.78 (215)	27,500		[*14*]	3.11 4.70		10.83	8.68	E.I.
9 	5.58 (222) 6.02 (206)	12,900 20,400	5.76 (216)	19,800		[*14*]	3.08 4.73	3.1	11.01	8.86	
10 	5.63 (220) 5.74 (216)	31,700 800	5.54 (224)	25,200		[*3*]	3.09 4.65		10.55		
11 	5.45 (228) 5.84 (212)	14,200 18,300				[*3*]	3.00 4.63		10.62		
12 	5.50 (225) 5.92 (209)	15,000 17,900	5.71 (217)	22,900		[*3*]	3.06 4.65		10.68		
13 	5.65 (219) 5.71 (217)	32,900 0	5.60 (222)	22,000	cyclo-hexane	[*10*]	3.08 4.62		10.49		

Table 1 (continued)

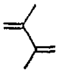
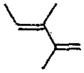
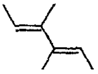
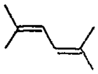
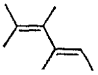
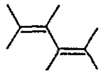
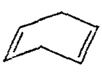
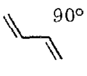
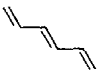
Compound[a]	Singlet Transitions						Triplet Transitions		Ionization Energy		
	Calc.		Obs.				Calc.	Obs.[d]	Calc.	Obs.	
	eV (mμ)	ε[b]	eV[c] (mμ)	ε	Solvent[j]	Ref.	eV	eV	eV	eV	Method[e]
14 	5.70 (218) 5.79 (214)	0 33,400	5.64 (220)			[*14*]	3.04 4.66		10.89	8.72	
15 	5.59 (222) 5.65 (219)	0 32,500	5.44 (228)	22,900	cyclohexane	[*10*]	2.99 4.58		10.52		
16 	5.48 (226) 5.54 (224)	0 32,100					2.94 4.48		10.17		
17 	5.44 (228) 5.60 (221)	31,300 0	5.20 (239)	24,000		[*10*]	3.04 4.50		9.95		
18 	5.40 (230) 5.43 (228)	7,100 24,200					2.90 4.41				
19 	5.32 (233) 5.33 (233)	30,900 0	only end absorption above 210 mμ			[*10*]	2.87 4.34		9.64		
20 	5.21 (238) 5.71 (217)	14,200 1,300	4.96 (250) 6.02 (200)	5,200 5,400		[*20,23*] g,h	3.01 4.61	2.9	10.57	8.40	S
21 	6.42 (193) 7.37 (168)	0 28,800	6.20 (200)			g	4.07		10.91		
22 	7.37 (168) 7.83 (158)	25,400 15,000					4.40 7.86		12.77		
23 	4.98 (249) 5.14 (241) 5.94	0 49,600 0	5.09 (244)	53,000[i]		[*13,23*]	2.66 4.13 5.18	2.6	10.60	8.26	S

Table 1 (continued)

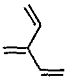
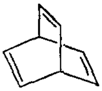
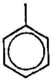
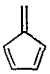
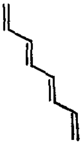
	Singlet Transitions						Triplet Transitions		Ionization Energy		
	Calc.		Obs.				Calc.	Obs.[d]	Calc.	Obs.	
Compound[a]	eV (mμ)	ε[b]	eV[c] (mμ)	ε	Solvent[j]	Ref.	eV	eV	eV	eV	Meth-ode[e]
23	(209)										
	7.27 (171)	0									
24 	5.31 (234)	12,100					2.99 3.98		10.90		
	5.40 (230)	1,700					5.01				
	6.10 (203)	1,700									
	6.44 (193)	31,300									
25 	5.99 (207)	0	5.19 (239)	300	EtOH	[*29*]	4.09		10.32		
	6.01 (206)	0	5.97 (208)	1,100	EtOH	[*29*]					
	7.08 (175)	8,800									
26 	4.66 (266)	0	4.90 (253)	234		[*3*]	4.15 4.64	3.9	12.39 (9.47)[f]	9.24	
	5.76 (215)	0	6.19 (200)	6,300		[*3*]	5.67				
	7.27 (171)	85,500	6.94 (179)	120,000		[*3*]					
27 	4.61 (269)	300	4.73 (261)	213		[*3*]	4.12		12.10	8.82	
	5.69 (218)	0	6.08 (204)	7,800	*n*-heptane	[*14*]					
	7.20 (172)	82,100	6.78 (183)	55,000	*n*-heptane	[*14*]					
28 	2.96 (418)	400	3.32 (373)	280	EtOH	[*24*]			11.18		
	5.06 (245)	8,300	5.21 (238)	14,500	EtOH	[*24*]					
	6.21 (197)	15,800									
29 	4.54 (273)	0	4.61 (269)			[*8*]	2.55 3.72	2.2	10.25	7.8	S
	4.74 (262)	65,100									
	5.49 (226)	500									
	6.15 (200)	0									

Table 1 (continued)

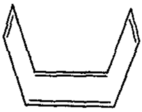
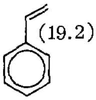
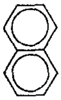
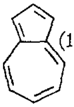
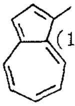
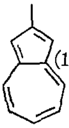
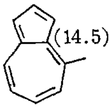
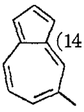
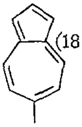
	Singlet Transitions						Triplet Transitions		Ionization Energy		
	Calc.		Obs.				Calc.	Obs.^{d}	Calc.	Obs.	
Compound^a	eV (mμ)	ε^b	eV^c (mμ)	ε	Solvent^j	Ref.	eV	eV	eV	eV	Method^e
30 	5.48 (226)	0	4.43 (280)	280	iso-octane	[3]			12.01	8.6	
	6.71 (185)	100									
	7.76 (160)	71,700									
31 	4.53 (274)	0	4.43 (280)	800		[3]	3.45		11.34	8.35	
	5.10 (243)	12,900	5.21 (238)	10,000		[3]					
	6.25 (198)	0	6.33 (196)	68,000		[3]					
	6.35 (195)	14,200	6.89 (180)	30,000		[3]					
	6.66 (186)	31,300									
32 	4.27 (290)	1,700	4.11 (302)	270	iso-octane	[3]	3.53 4.24		11.18	8.12	
	5.01 (248)	4,200	4.61 (269)	5,600^i		^{g}					
	6.61 (188)	99,700	5.88 (211)	120,000^i		^{g}					
33 	1.97 (629)	700	2.14 (580)	350	pet. ether	[21]	1.96 2.49		10.29	7.72	E.I.^{k}
	3.55 (349)	200	(see Fig. 1)								
	4.43 (280)	9,900									
	4.68 (265)	13,800									
34 	1.83 (677)	700	2.04 (608)	260	pet. ether	[21]			10.08		
	3.29 (377)	600									
	4.40 (282)	6,000									
	4.44 (279)	3,300									
35 	2.06 (602)	600	2.18 (569)	260	pet. ether	[21]			10.29		
	3.40 (365)	0									
	4.32 (287)	3,800									
	4.74 (262)	23,800									

Table 1 (continued)

	Singlet Transitions						Triplet Transitions		Ionization Energy		
	Calc.		Obs.				Calc.	Obs.[d]	Calc.	Obs.	
Compound[a]	eV (mμ)	ε[b]	eV[c] (mμ)	ε	Solvent[j]	Ref.	eV	eV	eV	eV	Meth-od[e]
36  (14.5)	2.04 (608)	800	2.18 (568)	430	pet. ether	[21]			10.25		
	3.39 (366)	300									
	4.42 (281)	3,800									
	4.70 (264)	1,700									
37  (14.5)	1.90 (653)	800	2.09 (592)	360	pet. ether	[21]			10.16		
	3.34 (371)	400									
	4.42 (281)	6,700									
	4.48 (277)	4,600									
38  (18.0)	2.02 (614)	500	2.19 (565)	340	pet. ether	[21]			10.25		
	3.44 (360)	100									
	4.33 (286)	3,800									
	4.76 (261)	23,300									

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[a] The geometrical isomers pictured for compounds 12, 13, 15 and 29 may not be those on which the experimental determinations were made. Values in parentheses indicate truncation point in eV.

[b] Oscillator strengths were converted to extinction coefficients by fitting ethylene: $\varepsilon = 41{,}700\,f$.

[c] Corrected to vapor phase by the method of Ref. [4] using molar refractivities from Ref. [27] in place of cavity radii. Transition energies were chosen at $\lambda_{\max}$ for unstructured spectra and at the vibrational maximum position closest to the center of the integrated absorption intensity (by inspection) for vibronically structured spectra.

[d] See ref. [8].

[e] Photoionization determinations were used when available, and unless otherwise designated by S = Spectroscopic and E.I. = Electron Impact. Electron Impact values tend to be 0.1—0.3 eV higher. From Ref. [16], except where noted.

[f] See text.

[g] Determined in this laboratory.

[h] The extinction coefficient for this transition in the gas phase is slightly higher than for the low energy transition, and is estimated by comparison with Ref. [20]. However, the relative oscillator strengths are not well represented by the extinctions, for this band consists of several sharp peaks, whereas the first is broad.

[i] In isooctane.

[j] Experimental spectra are for the gas phase if no solvent is mentioned.

[k] See Ref. [26].

which experimental data are available (all but 11, 16 and 18) the errors are generally less than 0.1 eV, and never more than 0.15 eV, except for the hexamethylated compound (19) which has recently been prepared and had its spectrum described [*10*]. Here it is not possible to compare the experimental and calculated value, since it is clear from the form of the experimental spectrum that the compound is actually non-planar, but to an unknown degree. The calculated values apply to planar systems. The calculated values may be compared indirectly with the values predicted by Woodward's rules [*28*], which apply to cyclic, and therefore planar, systems. The calculated values obtained here are in good agreement with those obtained via Woodward's rules. It should in fact be possible to calculate the degree of non-planarity from the experimental data, although this has not been done in the present work.

Compound number 21 is a special non-planar case, in which the double bonds are not conjugated, but are rather near together in space. The first transition is found experimentally at 6.20 eV, and the calculated value is 6.42 eV. An intense extinction at shorter wavelength has been noted experimentally, and it continues to increase down to 180 millimicrons, but the maximum was not reached. The calculated value for the strongly allowed transition is 168 millimicrons.

The linear *s-trans-s-trans*-hexatriene (number 23) is predicted to have one strong absorption band at 5.14 eV, as observed. Three additional transitions in the readily observable region are predicted, but they are all forbidden. Entry number 24, a cross-conjugated triene, is an interesting case. The experimentalist would regard this system as the sum of a *cisoid* diene and a *transoid* diene, and the calculated spectrum shows that this is in fact a good approximation. There are two strongly allowed transitions, a long-wavelength one (5.31 eV) with the oscillator strength typical of a *cisoid* diene, and a short-wavelength band (6.44 eV) with the much greater oscillator strength characteristic of a *transoid* diene. In addition there are the weaker bands as noted.

Compound 25 (barrelene) does not have a calculated spectrum in very good agreement with that which is reported. The difficulty may be in part due to the inadequacy of the experimental spectrum, which has not been pictured in the literature, and which is described in an incomplete fashion and only for the compound in solution [*29*].

For benzene, the third transition, which is the first allowed one, is predicted at 7.27 eV, while the experimental values reported range from 6.76—6.94 eV, corresponding to an error of 0.33 eV or more. The first transition is calculated with greater accuracy, but the middle transition deviates by 0.43 eV. This band has generally given difficulties in calculation.

For toluene (entry number 27) the long-wavelength transition which is forbidden in benzene becomes allowed, although weak. All three transitions show red shifts relative to benzene, as would be anticipated.

Fulvene (entry 28) is calculated to have a spectrum which is qualitatively like that observed, but the first transition is off by 0.4 eV. This particular molecule (and the related heptafulvene as noted earlier [*1*]) has its first transition energy highly dependent upon the exact geometry chosen for the system, and by variations of 0.013 Å in different bond lengths, the calculated spectrum may be brought into agreement with experiment. Since the actual geometry of the molecule is not

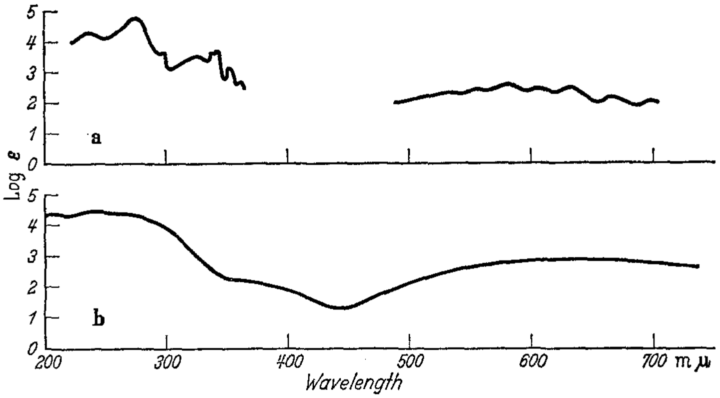


Fig. 1. The experimental (a) and calculated (b) spectra of azulene in petroleum ether

known, the agreement (or lack of it) between the calculated and experimental values does not appear to be of great significance at the present time. The sensitivity of the calculated spectrum to the exact structure points out a need for better methods of accurately calculating the structure.

Compound 29, the linear octatetraene, again has its spectrum calculated satisfactorily. The numerous reported bands are known to result from vibrational transitions, and all belong to a single electronic transition.

Stryrene (entry 31) has a rather complicated spectrum, both experimentally and by calculation, and the agreement is good.

Azulene (entry number 33) has its first transition within 0.2 eV of the experimental value. The second and subsequent transitions cannot be identified with certainty in the experimental spectrum, so we have plotted the spectrum as shown in Fig. 1. Since the methyl derivatives of azulene show the low energy transition shifted in various directions depending upon the position of methylation, it was of extreme interest to see whether or not these shifts could be adequately calculated. Since the transition in question is off by 0.2 eV in azulene itself, similar errors will be anticipated for the methyl derivatives, and the calculated spectra, together with the experimental ones, are listed in Tab. 1 (entries 34—38). To facilitate comparison, the calculated and experimental shifts relative to azulene itself (for the low energy transition) are summarized in Tab. 2. The agreement appears to be satisfactory.

It might be mentioned that the configuration interaction matrix for azulene itself, and for the symmetrical azulenes, factors in two. By keeping 110 configurations in each matrix, the configuration interaction can be carried up to an energy of 18.0 eV above the ground state. The unsymmetrical azulenes have a configuration interaction matrix which does not factor, and hence the same 110 configurations in a single matrix allow only those up to an energy of 14.5 eV to be kept. The amount of error introduced by truncating the configuration interaction matrices at 14.5 eV instead of 18.0 eV was studied by truncating the matrices from the symmetrical molecules at the appropriate energy, and it was found that spectral shifts of up to 0.06 eV were obtained in this way.

Table 2. *Spectral Shifts of Methylated Azulenes*

Shift From		1-Me	2-Me	4-Me	5-Me	6-Me
Azulene (mμ)	Calc.	+46	−27	−21	+24	−15
	Obs.	+28	−11	−12	+12	−15

We can summarize the situation up to this point by saying that there do not appear to be any errors between calculation and experiment for the compounds so far discussed of more than 0.4 eV which can be definitely attributed to shortcomings in the calculation. Such few errors of this size as do exist may well be attributable to the inadequacy of the experimental data. However, this is not true for all of the transitions in the compounds which follow: In naphthalene (entry 32), the first two transitions are well calculated with regards to both energy and oscillator strength. The oscillator strength of the third transition is adequately calculated, but the energy is in error by 0.7 eV. We carefully redetermined the spectrum of naphthalene in the gas phase, and this error is definitely not an experimental one.

Finally, cyclooctatetraene (entry 30) is calculated to have transitions at 5.48 eV (forbidden), at 6.71 eV (very weakly allowed), and at 7.76 eV (strongly allowed). The experimental spectrum was determined in the gas phase, and the compound shows a weak broad band at 4.43 eV, followed by increasingly strong absorption down to 5.64 eV, which is as far as the experimental measurements were carried out. Thus there seems to be a discrepancy between the calculated and experimental transition energy for the first band of approximately 1 eV. The geometry of this molecule has recently been carefully determined [*25*], and variations in bond lengths and angles of the size attached to the experimental limits to which these things are known do not lead to a singnificant change in the calculated spectrum. On the other hand, at 77 °K the spectrum shows an apparent blue shift [*18*], and a broad, flat maximum between 4.4 and 4.9 eV.

The compounds considered here constitute a wide cross section of typical types of structures which are known experimentally, and we have deliberately chosen as broad a representative selection as possible. Clearly there is a very high degree of correlation between the calculated and experimental spectra. The standard deviation for 44 observed transitions is 0.35 eV, which may be compared with a probable average deviation of 0.1—0.2 eV for the experimental determinations. Exclusion of the three non-planar compounds results in a standard deviation of only 0.24 eV. It might be expected that this correlation with experiment weights the ethylenes and butadienes too heavily, but if one carries out the correlation on just the parent compounds (including the non-planar ones), the standard deviation is only slightly greater, 0.44 eV for 23 transitions.

We would like to focus our attention now on the transitions studied for which the calculated values differ from the experimental ones by more than what seems to be a reasonable experimental error (about 10% of the total number). There are really a total of four transitions in three molecules that we must consider; the long wavelength transition in cyclooctatetraene, the third transition in naphthalene, and the first two transitions in barrelene. While any one of these might be passed off as a freak, taken together these errors indicate that the calculation does in fact fall short of what we would desire. At least two of the three molecules in question are atypical ones from a mathematical point of view, in that for both cyclooctatetraene and for barrelene, the doubly excited configurations interact strongly with the ground configuration, but weakly (cyclooctatetraene) or not at all (barrelene) with the singly excited configuration which contributes the largest amount to the terminus state of the transition in question. For these two molecules, the results would have been better if doubly excited configurations had been omitted from the configuration interaction. This leads us to wonder if perhaps one should as a matter of principle include triply-excited configurations in the calculation. When doubly-excited configurations are included, all of the direct interactions of the ground state with other configurations are taken into account, since triply- and higher-excited configurations cannot interact directly with the ground state. Triply-excited configurations can, however, interact with the singly-excited states including the one which is the terminous of the transition of interest. Hence by omitting the inclusion of the triply-excited configurations, one is treating somewhat unequally the ground and singly-excited configurations, and this unequalness may not cancel out very well when a range of molecules is considered. There is reason to think, as mentioned above, that cyclooctatetraene and barrelene would be cases in which the deficiency might well show up to a very great extent. The triply-excited configurations in such molecules generally range from about 15 to 25 eV above the ground state, but a number of them are within 10 eV or so of the singly-excited state with which the interaction is concerned.

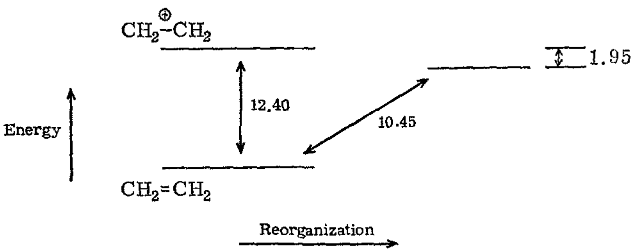
It also must be pointed out that these two molecules differ in an extreme way from planar systems, and the σ-π separation may be a poor approximation here. We feel it is desirable to know what the effect of triply-excited configurations might be, however, and such studies are now underway and will be reported separately. To our way of thinking, the Pariser-Parr method really contains two important features (the empirical evaluation of certain integrals, and the omission of multicentered integrals), and to understand the validity of these approximations, one must also know something about the accuracy of the wave functions being employed. In other words, are the errors between calculation and experiment which we have found in the present work attributable to the Pariser-Parr approximations, or are they simply a result of using inadequate wave functions? We will have to postpone further discussion on this point.

Next we might briefly consider the singlet-triplet transitions for the molecules concerned. Here the experimental data are very sketchy indeed, and there is considerable danger that the transitions observed may not correspond to those for which the calculations are carried out. For example, the well-known "mystery band" in ethylene [22] may have analogs in the singlet-triplet series. The lowest lying singlet-triplet transitions calculated for ethylene, butadiene, isoprene, 1, 3-cyclohexadiene, hexatriene, benzene and octatraene are all in good agreement with experiment. The difficulty comes with the higher energy transitions. Our earlier calculations [2], which included only singly-excited configurations in the treatment of the triplet states, always gave singlet-triplet transitions other than the lowest one at too high an energy, and it is now found that addition of the doubly-excited configurations does not significantly improve matters. As noted above, there is a serious difficulty in locating the band centers for these transitions, but invariably there are errors on the order of 1 eV between the calculated and experimental (0, 0) values. It is improbable that the band center is this far away. It seems more likely to us that these observed transitions do not correspond to the π-π^* transitions for which the calculations were carried out, which presumably occur at still higher energies, and have not actually been observed. In view of the uncertainty as to the nature of the experimental transitions, this question will not be pursued further at this time. It is possible that the triply-excited configurations here might bring the calculations into better agreement with experiment, but it does not seem likely that such large shifts would regularly result for the second and not the first singlet-triplet transitions. The amount of effort in programming for such calculations seems to be too large an investment for the probable results that will be obtained, and we do not intend to pursue this aspect of the problem.

Finally, we examined the calculated and experimental ionization potentials of the molecules. If we refer to the methylated ethylenes (entries 1—6, Tab. 1), we note that the *trend* is predicted to within 0.1—0.2 eV. The absolute numbers given by Koopman's theorem are 1.9—2.1 eV too large when compared with the experimental numbers, however. Again, if we look at the series of dienes, or the aromatics, we see that generally the trends are predicted quite well, but the absolute numbers are always off by 2—3 eV.

The variation of the ionization potential of a substituted ethylene with the substitution has been interpreted as indicating a σ, rather than a π electron, was being removed [*5*]. The present work indicates that no such interpretation is required.

While our VESCF treatment is designed to deal well with the ground state, it contains the assumption that the electron distribution in the excited states will not differ so much from that of the ground state as to invalidate using the same orbitals and attendant data for both. Certainly one cannot expect that the ion which results from complete removal of an electron from the molecule will be very closely approximated by the VESCF ground state. While it would be possible to treat these open-shelled ions by a VESCF treatment, we are not prepared to carry out such calculations at this time. Qualitatively, however, it is clear what will happen, within the framework of the VESCF method. When an electron is removed from the system, the nuclear charges on the atoms will increase, depending on the distribution of the electron removed, and the ionization potentials for the atoms will similarly increase, and the various other dependent parameters will change accordingly. This reorganization of the π system will result in its contraction, that is to say, the effective nuclear charges in the molecule as a whole will be increased, the remaining π electrons will be pulled in more closely, and the energy of the ion will be lower than that calculated using the ground state orbitals. If we properly carried out a VESCF treatment on this open-shelled ion, its energy would be reduced, and hence the ionization potentials calculated would be lowered. Qualitatively, the calculated ionization potentials are too high, so that this is the type of effect we need to improve the agreement between calculation and experiment. We have carried out the calculation by hand in two cases, for benzene and for ethylene, as in these two cases the orbitals are determined by symmetry, and one does not need to do an open-shelled VESCF calculation. An outline of the results of the calculation in the case of ethylene may be sketched as follows:



Clearly, then, when the VESCF method is applied properly to the ion, and the ionization potential is taken as the difference in energy between the molecule and the ion, the agreement is practically perfect for ethylene. Similarly, the calculation was carried out for benzene, and it was found that the calculated ionization potential listed in Tab. 1 was lowered by 2.92 eV. Again, the ionization potential calculated with this refinement is practically perfect. Qualitatively, it is clear that one will have a 2—3 eV lowering in the ionization potential when the ion itself is properly treated by this method. Since both ethylene and benzene give good results, and the trends are correct, it is apparent that with such a refinement the ionization potentials of the molecules listed in Tab. 1 could, in general, be accurately calculated by this method. We note that no previous calculations, which properly include penetration effects, have given these ionization potentials correctly.

Appendix

The bond lengths for most compounds were determined from the bond order — bond length relationship of Dewar and Schmeising [*7*]. A self-consistent approach was applied until deviations were less than 0.002 Å. Bond angles of 120° were assumed. In the cases of the butadienes and cyclooctatetraene the electron diffraction data of Traetteberg [*25*] was used, and the naphthalene values came from the work of Cruickshank and Sparks [*6*]. 1,4-Cyclohexadiene coordinates were calculated by assuming bond lengths of 1.334 Å and 1.501 Å, bond angles of 120° at the unsaturated carbons and 110° at the saturated centers, and a boat conformation where the saturated carbons are 29° above the plane of the π-systeme. The geometry for barrelene is described in Ref. [*1*].

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