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Organic Quantum Chemistry. IX. The Ultraviolet Spectra of Unsaturated Hydrocarbons. Woodward's Rules^{1,2}

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Using a modified version of the Pariser-Parr method which allows for induction in the σ -system, the singlet and triplet transitions have been calculated for a variety of unsaturated hydrocarbons, including ethylene and methylated ethylenes and cis- and trans-butadiene and methylated derivatives. A configuration interaction treatment including all singly excited configurations was carried out in the case of the triplet transitions, while for the singlet transitions, doubly excited configurations were also included. Calculated and observed transitions agree to within a few millimicrons in most cases. A quantitative theoretical basis for Woodward's rules in these compounds is established.

Introduction

In 1942 Woodward introduced a set of empirical rules by the application of which one could rather accurately predict the location of the maximum absorption in the ultraviolet spectrum for any ordinary planar conjugated diene.³ These rules and their extensions are limited in their area of applicability to nearly planar compounds which are not cross-conjugated, but within these limitations they are quite accurate for predictive purposes. It seemed amazing to the present authors that with the great strength of modern theoretical organic chemistry available, and with the easy accessibility of large, fast electronic computers to carry out numerical calculations, up until

now Woodward's rules have offered more accurate predictions (within their area of applicability) than any other methods. The present paper is primarily concerned with the practical application of available theoretical principles to the solution of the spectral prediction problem for unsaturated hydrocarbons. The immediate goal is to duplicate the results of Woodward's rules for hydrocarbon systems, and to do so in a general way so that one would not be limited to systems of any particular geometry. In a previous paper,⁴ the π -electronic spectra were calculated for a number of dienes and trienes, conjugated, unconjugated, and cross-conjugated, utilizing the basic method of Pariser and Parr.⁵ The calculations were done for the "stripped chromophore," and the effect of substituents had to be taken into account utilizing Woodward's rules.

The results obtained agreed quite well with the observed spectra in most cases for the singlet transition energies, although for *s-cis*-polyenes the agreement was poor. The triplet transition energies in general were found to be unsatisfactory. The objective of this paper was to expand the earlier method by explicitly accounting for the inductive effect in the σ -system, and to predict the shift in the position of maximum absorption due to alkyl substitution. It was found that the new method also overcame the two principal deficiencies of the earlier method and brought both the *s-cis*-polyenes and the $N \rightarrow T_1$ transitions into agreement with experiment.

We begin by assuming a σ - π separation for polyenes, and will treat explicitly only the π -electrons in the

(1) Paper VIII: N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **87**, 1227 (1965).

(2) Supported by Grant No. DA-ARO-D-31-124-G494 from the Army Research Office.

(3) (a) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942); (b) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 15.

(4) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **86**, 2811 (1964).

(5) R. Pariser and R. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

potential field of the σ -system. Because of the inductive effects of the σ -system, the electron densities about the different atoms in a molecule in general differ markedly from one another, and from those in the free atoms. In constructing the core Hamiltonian, therefore, one must use ionization potentials for the atoms with the effective nuclear charges they have in the molecule, rather than using the ionization potentials of the free atoms. The inadequacy of the latter has been discussed by Sidman.⁶ There are various ways in which the inductive effect of the σ -system might in principle be approximately taken into account; perhaps the best one so far used is the "core and peel" method,⁷ but this approach appears to be too complicated to extend conveniently at this time to the larger molecules we wish to study. Another previously used approach is that referred to as the VESCF (Variable Electronegativity Self-Consistent Field) method of Brown and Heffernan.⁸ We have used some of the ideas of this method, but have proceeded *via* a configuration interaction scheme rather than by the SCF approach, since we wish to push the accuracy of the treatment beyond that obtainable by single determinantal wave functions. The main feature of the method adopted in this work was to allow for the inductive effects of the σ -system through the different effective charges (or orbital exponents) of similar orbitals in different environments, the difference from the atomic value being estimated by comparing experimental ionization potentials of free radicals related to the particular case at hand. The effective ionization potentials and various integrals corresponding to the estimated effective charges are then used instead of the atomic valence state values.

Two additional significant modifications were made in the earlier method. One concerns the evaluation of the resonance integrals. The approach most consistent with the method is to include them between all pairs of p-orbitals, neighboring or otherwise. The omission of these terms for interactions between non-neighbors is a holdover from the days of hand calculation and does not appear justifiable now. We found that inclusion of these nonneighbor resonance integrals shifted the calculated spectra of cisoid dienes so that they are no longer anomalous.

The second modification of the basic method which we have now added is the inclusion of doubly excited configurations in the configuration interaction treatment. This inclusion in principle improves considerably the accuracy of the method; the practical outcome will be discussed below. Some additional modifications were also made in the methods used to evaluate repulsion and resonance integrals as discussed below.

Method of Calculation

The Interdependence of Ionization Potential and Nuclear Charge. The basis for the present treatment is the modified⁴ ASMO-CI method of Pariser and Parr,⁵ which was further modified here by inclusion of the inductive effects of the σ -system, which changes the effective nuclear charges (Z) of the nuclei in the core,

(6) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

(7) J. M. Parks and R. G. Parr, *ibid.*, **32**, 1657 (1960).

(8) R. D. Brown and N. L. Heffernan, *Australian J. Chem.*, **12**, 319 (1959).

which in turn changes the ionization potentials (I) which appear in the core integrals. Assuming for the moment that Z for an atom in a molecule is available, it is necessary to know the dependence of I on Z . The equation relating these two quantities was therefore evaluated for carbon in its appropriate valence state, using a method similar to that described by Brown and Heffernan.⁸ Atomic valence-state ionization potentials for a series of isoelectronic atoms or ions were calculated from atomic spectroscopic data.⁹ Since the ionization potential is a measure of the attraction of an electron for the nucleus, it is related to the nuclear attraction integral, which in turn is (to a good approximation) linearly proportional to the nuclear charge. For the same effective charge Z , the ionization potentials $I_C(Z)$ and $I_X(Z)$ corresponding to different nuclei with charges C and X , respectively, are related by

$$I_C(Z) = [I_X(Z)](C/X) \quad (1)$$

Consequently the ionization potential $I_X(Z)$ is corrected by a factor of C/X for use of evaluating the function $I_C(Z)$.

In Table I are given the experimental ionization potentials (I_X) and the nuclear charges (Z) of a series of ions isoelectronic with carbon. The last column gives

Table I. Ionization Potential As a Function of Nuclear Charge^{a,b}

	Z	X	I_X	I_C
$B^- \rightarrow B$	2.25	3	1.07	1.429
$C \rightarrow C^+$	3.25	4	11.54	11.54
$N^+ \rightarrow N^{2+}$	4.25	5	29.17	23.336

^a These are valence-state ionization potentials corresponding to the process $sxyz \rightarrow sxy$. ^b The nuclear charges of boron, carbon, and nitrogen are taken as 3, 4, and 5, respectively, since the two 1s electrons are considered as part of the atomic core.

the ionization potentials corresponding to the carbon nuclear charge. From the three values of Z first listed and I_C , a parabola was derived which described the variation of I with Z for carbon.

$$I_C(Z) = 0.8409Z^2 + 5.4861Z - 15.1718 \quad (2)$$

In Table II are given a list of pertinent molecules with their experimental ionization potentials and the effective charges calculated using eq. 2.

Table II. Experimental Ionization Potentials (I) and the Corresponding Charges (Z_C)^a

	I	Z_C
$C (sxyz \rightarrow sxy)$	11.54 ^b	3.250
$CH_3\cdot$	9.95 ^c	3.103
$CH_3CH_2\cdot$	8.78 ^d	2.993
$(CH_3)_2CH\cdot$	7.90 ^d	2.909
$(CH_3)_3C\cdot$	7.42 ^e	2.862

^a The free radicals are believed to be planar (footnote e) and hence these ionization potentials are vertical and correspond to the process $C(sp^2, sp^2, sp^2, \pi) \rightarrow C^+(sp^2, sp^2, sp^2)$. ^b See ref. 9. ^c F. P. Lossing, K. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954). ^d J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955). ^e F. P. Lossing and J. B. Sousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

Effective Charges Z. Once Z is known for each atom, straightforward application of eq. 2 gives the cor-

(9) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

responding I , and the calculation then follows the conventional path. The key to success, then, is the correct evaluation of the effective nuclear charges. Each sp^2 carbon has three neighbors which could be hydrogen, a methyl or alkyl group, or another sp^2 carbon. The sp^2 - sp^2 carbon-carbon bond is taken as nonpolar in all the molecules. The inductive effect of one or more hydrogen atoms or alkyl groups attached to one of the carbons was deduced from the data in Table II. Unfortunately, the relative importance of the inductive and hyperconjugative effects of a methyl group are not at all clear.¹⁰⁻¹² For present purposes it will be assumed that the methyls exert only an inductive effect or at least can be treated as if this were the case. The justification of this assumption will have to come ultimately from the agreement between the calculation and experiment.

To begin, the charge of the π -orbital of a carbon with two of its three sp^2 orbitals bonded to hydrogen atoms, and the other bonded to another sp^2 carbon, can be written as

$$Z_c(\text{H}_2\dot{\text{C}}-\text{C}) = Z_c(\text{H}_2\dot{\text{C}}-\text{H}) + \Delta Z_c$$

where ΔZ_c is the change in $Z_c(\text{H}_2\dot{\text{C}}-\text{H})$ due to the absence of the H bonded to the carbon. From Table II, the substitution of the last methyl group for a hydrogen in the substituted methyl radical changes Z_c by an amount of -0.047 unit out of a total of -0.241 (the difference between $Z_c(\text{Me}_3\text{C}\cdot)$ and $Z_c(\text{H}_3\text{C}\cdot)$). Assuming that the last hydrogen of the methyl radical contributes the same fraction of the total of -0.147 , the difference between $Z_c(\text{C})$ and $Z_c(\text{Me}\cdot)$, then $\Delta Z_c = 0.147 \times 0.047/0.241 = 0.029$. Hence $Z_c(\text{H}_2\dot{\text{C}}-\text{C}) = 3.132$. For carbon atoms bonded to two carbon atoms and one methyl group, Z_c is calculated as

$$Z_c(\text{Me}\dot{\text{C}}\text{C}_2) = Z_c(\text{Me}-\dot{\text{C}}\text{Me}_2) + \Delta Z_c'$$

where $\Delta Z_c'$ is the effect of the second and third methyl groups in the $\text{Me}_3\text{C}\cdot$ radical. It is found (Table II) that the last two methyl substitutions of the radical changes Z_c by -0.131 unit out of a total of -0.211 ; therefore $\Delta Z_c'$ is approximated as $\Delta Z_c' = [Z_c(\text{C}) -$

Table III. Parameters of the Carbon Orbitals

Orbital	Z	I	$\gamma_{C_\pi C_\pi}$ (theor.)	$\gamma_{C_\pi C_\pi}$ (emp.)
$\text{H}_2\dot{\text{C}}-\text{C}$	3.132	10.25941	16.67445	10.67771
$\text{MeH}\dot{\text{C}}-\text{C}$	3.022	9.08670	16.08882	10.30270
$\text{Me}_2\dot{\text{C}}-\text{C}$	2.938	8.20488	15.64162	10.01632
$\text{H}\dot{\text{C}}\text{C}_2$	3.183	10.81003	16.94597	10.85158
$\text{Me}\dot{\text{C}}\text{C}_2$	3.073	9.62788	16.36034	10.47657
$\dot{\text{C}}\text{C}_3$	3.250	11.54000	17.30267	11.08000

$Z_c(\text{Me}_3\text{C}\cdot)] \times 0.131/0.241 = 0.211$; hence $Z_c(\text{Me}\dot{\text{C}}\text{C}_2) = 3.073$. The orbital exponents for variously substituted carbon atoms were found in this way and are given in Table III.

(10) Conference on Hyperconjugation, Collected Papers, *Tetrahedron*, **5**, 105-274 (1959).

(11) S. Ehrenson, *J. Am. Chem. Soc.*, **84**, 2681 (1962).

(12) R. L. Flurry, Jr., and P. G. Lykos, *ibid.*, **85**, 1033 (1963).

Repulsion Integrals. The one-center repulsion integrals are obtained from the atomic spectral data as the difference between the valence-state ionization potential and the electron affinity. Since the theoretical one-center repulsion integrals are proportional to the effective charge Z , and since the atomic spectral values correspond to Slater Z 's, the data thus obtained are corrected by a factor Z_a'/Z_a , where Z_a' is the effective charge of an orbital centering on "a" when "a" is in a molecule, and Z_a is its Slater value. For example, $\gamma_{cc}(Z') = \gamma_{cc}(Z)(Z'/Z)$. For carbon with Slater Z , $\gamma_{C_\pi C_\pi} = 11.08$ e.v.

The two-center repulsion integrals are calculated according to the following equation⁷

$$\gamma_{ab}(\text{emp.}) = \gamma_{ab}(\text{theor.}) - \frac{1}{2}S_{ab}[\gamma_{aa}(\text{theor.}) - \gamma_{aa}(\text{emp.}) + \gamma_{bb}(\text{theor.}) - \gamma_{bb}(\text{emp.})]$$

where S_{ab} is the overlap integral over orbitals a and b. The one-center repulsion integrals are given in Table III.

Core Integrals. The values for α are obtained in the usual way using the Goepfert-Mayer and Sklar approximation,⁵ except that the penetration integral terms are omitted since the current procedure of evaluating ionization potentials has in fact taken into account the penetration effects.

The resonance integrals are evaluated between all of the orbitals of the π -system, neighboring or otherwise, using Mulliken's formula

$$\beta_{pq} = \frac{(I_p + I_q)S_{pq}/(1 + S_{pq})}{(I_r + I_s)S_{rs}/(1 + S_{rs})}(\beta_{rs})$$

The $C_\pi C_\pi$ bond of cyclohexene was chosen as a standard. The cyclohexene π -orbitals were approximated by those in *cis*-2-butene with $Z_c = 3.022$. A satisfactory fit to the $\pi \rightarrow \pi^*$ transition is found with $\beta_{rs} = \beta_{CC}$ equal to -2.700 e.v.,¹³ and this is the only completely arbitrary parameter used in this treatment. Substituting values for β_{rs} , S_{rs} , I_r , and I_s pertaining to the cyclohexene π -bond into the above equation¹⁴

$$\beta_{pq} = -0.61706(I_p + I_q)S_{pq}/(1 + S_{pq}) \quad (3)$$

Method of Computation. The starting MO's were obtained by diagonalization of Hückel matrices with elements calculated according to a modification of the formula of McWeeny and Peacock.¹⁵ The equation for calculating the diagonal elements was simplified to

$$\alpha_x = (I_x - I_s)/9.58 \quad (4)$$

where I_x and I_s are the ionization potentials of any orbital "x" and a standard orbital "s," respectively. The off-diagonal elements are proportional to the resonance integral β 's, with β (Hückel units) = $\beta(\text{e.v.})/(-2.402)$. From this point one might proceed by the VESCF method. We have not followed that path, since our description of the system of interest at this point does not differ very much from the VESCF description, and in any case we do not wish to confine ourselves to a single determinantal wave function. The configuration interaction method was employed.

(13) As discussed below, the recommended value for this integral is -2.619 e.v.

(14) As discussed below, the recommended value for the constant in eq. 3 is -0.59855 .

(15) R. McWeeny and T. E. Peacock, *Proc. Phys. Soc. (London)*, **A70**, 41 (1957).

The basic programs were described earlier.⁴ Another program was written to calculate the configuration matrix interaction elements between all doubly excited configurations with the ground and singly excited configurations, and each other.¹⁶ Except where otherwise noted, the configuration interaction treatment for each triplet state included all singly excited triplet configurations, and that for each singlet state included the ground configuration together with all singly and doubly excited singlet configurations.

At the present time, with the computer available to us (IBM-7070) and the programs described, a doubly excited treatment for molecules much larger than hexatriene cannot be undertaken, not because of the time involved (the running time for the treatment of hexatriene was 30 min.), but because of the limit of the storage capacity of the computer having been reached. By some manipulations of the programs to utilize the storage capacity more effectively, it would be possible to increase the size of the molecule that could be studied somewhat, but we are nearing the point where round-off error in the computations is becoming serious, a shift to double-precision computations will soon be required, and the running time will then increase substantially. Hence, it would appear that unless a computer with much larger storage and/or one which is much faster becomes available, the extension of these methods to handle really sizable systems (say 10 to 25 carbon atoms) is not practical at present.

Results

In Table IV are given the calculated wave lengths predicted for the $\pi \rightarrow \pi^*$ transitions by the present

Table IV. Calculated and Observed Spectra of Substituted Ethylenes

Compound	Transition, $m\mu$		Ref.
	Calcd.	Obsd. ^a	
$\text{CH}_2=\text{CH}_2$	164.0	170.3	<i>b,c</i>
$\text{CH}_3\text{CH}=\text{CH}_2$	170.0	175	<i>c</i>
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	176.8	188	<i>c</i>
$\text{CH}_3\text{CH}=\text{CHCH}_3$	175.5	175.5 ^d	
		176 (<i>cis</i>)	<i>c</i>
		179 (<i>trans</i>)	
		181	<i>c</i>
$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	186.4	187	<i>c</i>




















^a See ref. 17. ^b P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23**, 1895 (1955). ^c J. C. Jones, Jr., and R. W. Taylor, *Anal. Chem.*, **27**, 228 (1955). ^d Observed value of cyclohexene.

method for ethylene and its methyl derivatives together with the experimental values.¹⁷ The agreement is

(16) R. G. Parr, "The Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 25.

(17) The interpretation of the experimental data for many olefin spectra is not unambiguous. Depending on the vibrational fine structures and shapes of the bands, the maxima of the bands and their centers of gravity do not usually coincide, nor are these positions related in any simple way. In the present paper we have chosen the position of maximum absorption as the "wave length" of the band; although examination of the actual spectra indicates this is probably not the best interpretation, it is unbiased. Much of the interpretative difficulty disappears in solution spectra. Since many or even most organic compounds whose spectra might be of current interest cannot be conveniently examined in the gas phase, it is of practical importance to extend the present work to studies in the liquid phase, and this will be done in a subsequent paper. For the present we will simply note that disagreements between theory and experiment here may often be due to the difficulty of deducing the experimental value from the actual spectrum.

Table V. Calculated and Observed Spectra of Some Substituted Butadienes

Compound	λ_m (vapor)			Ref.
	Calcd. ^a	Woodward's rules	Obsd.	
(1) 	203.2	204	209.4	<i>b</i>
(2) 	210.0	209	214.8	<i>b</i>
(3) 	210.0	209	216 210.5	<i>c</i> <i>b</i>
(4) 	208.5	209	215.5	<i>b</i>
(5) 	215.0	214	223	<i>c</i>
(6) 	215.9	214		
(7) 	213.1	214	220	<i>d</i>
(8) 	214.1	214		
(9) 	207.3	214	220	<i>b</i>
(10) 	214.7	219		
(11) 	217.7	224		
(12) 		224		
(13) 	225.6	229		
(14) 	227.9	234		
(15) 	227	240 ^e		
(16) 	235	245 ^e		
(17) 	238	245 ^e		
(18) 	240.3	250 ^e		
(19) 	240.3 ^f	250 ^e	250	<i>g</i>

^a For unsymmetrical molecules, the two longest wave length transitions have almost equal intensities. The observed absorption wave length probably corresponds to the average of the two calculated values: for (2) and (3) 207.9, 212.0 $m\mu$; (4) 196.7, 220.3; (5) 211.0, 219.0; (6) 205.5, 226.4; (7) 199.7, 225.6; (10) 212.6, 216.8; (13) 222.2, 229.0. ^b Footnote *c*, Table IV. ^c National Bureau of Standards, American Petroleum Institute Research Project 44, 1945. ^d I. N. Nazarov and M. V. Mavrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 472, (1959); *Chem. Abstr.*, **53**, 21613h (1959). ^e These values were obtained from the experimental value for cyclohexadiene. Further data are given in Table VII. ^f Actually calculated for 1,4-dimethyl-*cis*-butadiene (assuming planarity). ^g H. Schuler, E. Lutz, and G. Arnold, *Spectrochim. Acta*, **17**, 1043 (1961).

generally satisfactory, the average deviation between the calculated and experimental values being about 4 $m\mu$. The nature of the experimental absorption bands is such that the band maxima and their center of gravity do not coincide much more closely than this, and this is really as good agreement as can be expected.

It may be pointed out that in these calculations the geometry of the molecule is taken to be that of the ground state. Thus the Frank-Condon transitions, and not the 0-0 bands, are under investigation.

Table VI. Electronic Energies from Various Configuration Interaction Treatments for *trans*-Butadiene^{a,b}

Configu- ration ^c	Complete treatment 1	Including doubly excited configurations			Including singly excited configurations		
		1	2	3	1	2	3
V ₀	0(-88.61067)	0(-88.60456)	0(-88.59400)	0(-88.59646)	0(-88.17127)	0(-87.96348)	0(-88.12014)
V ₂₃	6.11753	6.16132	6.13669	6.17200	6.07474	7.20019	5.84348
V ₁₃	6.34481	6.37134	6.38973	6.62457	8.13070	9.27823	9.32931
V ₂₄	7.95817	8.16068	8.18606	8.30334	7.72790	7.75273	8.30960
V ₁₄	10.31761	10.46804	10.61774	10.34075	10.48830	11.66171	10.75870
V ₁₁₃₃	15.25854	15.38902	15.95719	15.60363			
V ₁₁₄₄	25.08354	24.15825	23.18166	25.32295			
V ₂₂₃₃	9.98452	10.04022	10.22301	10.07357			
V ₂₂₄₄	14.99232	15.08179	15.59412	15.42778			
V _{1234(A)}	12.39979	12.80068	11.96170	12.62778			
V _{1234(B)}	17.73241	17.86302	17.86557	17.83976			
V ₁₁₃₄	26.34545	23.96994	22.68636	25.26518			
V ₂₂₃₄	14.33523	14.38272	14.46633	14.99597			
V ₁₂₃₃	11.27211	11.26821	11.26069	11.26878			
V ₁₂₄₄	16.59699	16.60600	16.60125	16.60602			
V _{122,334}	18.21604						
V _{112,344}	22.40343						
V _{122,344}	19.86960						
V _{112,334}	21.12029						
V _{1122,3344}	26.89127						

^a Same starting data as in text, but $\beta_{13} = \beta_{24} = \beta_{14} = 0$. ^b The wave functions have the usual form (ref. 19), the first coefficient having the values 0.3862, 0.2784, and 0.5000 for runs 1, 2, and 3, respectively. ^c V₀ denotes the ground configuration, v_{ik} a conformation differing from V₀ by the excitation of an electron from orbital *i* to *k*, and V_{ijkl} has had one electron from each *i* and *j* excited to *k* and *l*.

In Table V are presented the results obtained for the butadienes. Experimental spectra are available for only a few of the compounds; many of them are not yet known.

It is possible to predict with some degree of confidence where the longest wave length absorption maximum in the ultraviolet will occur by utilizing Woodward's rules. The values obtained by these rules are also included in Table V for comparison purposes. It may be noted that the calculated values appear to be systematically lower than the experimental values by about 4 m μ . Now that these data are available, one can see that a value smaller by about 3% for the standard β which was arbitrarily chosen at the outset would bring the average calculated and experimental values into better agreement both for the dienes and for the ethylenes. We have not repeated the calculations for this change because an excessive amount of labor would be required. From the way β enters into the equation for the transition energies, it is clear that from its adjustment all the N \rightarrow V₁ transitions for the *s-trans*-butadienes and ethylenes would be shifted to longer wave length by about 4 m μ , and those for the *s-cis*-butadienes by about 6 m μ . The variation of the position of the ultraviolet maximum with methyl substitution which is predicted agrees quite well with what is found experimentally, and if the standard β for cyclohexene is changed as recommended, the actual numerical agreement is excellent. Thus we are now able to predict the effect of alkyl substitution on the position of absorption about as well as Woodward's rules can, and from the earlier study⁴ we believe that the present method is equally applicable to nonplanar and cross-conjugated systems.

Discussion

In the calculations concerning the substituted ethylenes, the configuration interaction up to and including doubly excited configurations corresponds to a complete configuration interaction treatment. The results

are therefore the best one can do using the basis wave functions chosen within the framework of the method. With the dienes, there are a substantial number of configurations which must be taken into account at this level of approximation, and even so this does not correspond to a complete treatment. Since we are very interested in extending these calculations to larger systems, we were especially interested in knowing how the completeness of the configuration interaction treatment determined the accuracy of the results, and we therefore examined *trans*-butadiene in some detail.

trans-Butadiene. A comparison has been made of the results obtained from the McWeeny-Peacock-type orbitals when the configuration interaction was limited to inclusion of the ground state and (a) singly excited configurations, (b) singly and doubly excited configurations, or (c) all excited configurations.¹⁸ The McWeeny-Peacock orbitals that were used as starting orbitals (run 1 in Table VI) correspond rather closely to the SCF orbitals. To determine the importance of accurate starting orbitals, the calculation was also repeated using two sets of orbitals differing somewhat in opposite directions. For butadiene, there are four singly excited and ten doubly excited configurations which must be included in the calculations. The complications rapidly mount with molecular size, and in a hexatriene there are nine singly excited configurations and forty-five doubly excited ones, leading to a configuration interaction matrix which, allowing for the fact it is Hermitian, contains 1540 elements. Hence it does not seem feasible at the present time to try to include configurations which are higher than singly excited for molecules very much bigger than hexatriene. The results for butadiene are summarized in Table VI. The corresponding energy levels from any set of starting

(18) A similar but less complete examination of this molecule was made earlier by Moser.¹⁹ His procedure utilized a perturbation treatment of selected interactions. The availability of a computer now makes it possible to do the entire calculation in a proper way.

(19) C. M. Moser, *J. Chem. Soc.*, 3455 (1954).

orbitals are the same to within 0.0004 e.v. when the complete treatment is carried out, which serves as a check on the programs.

Starting with the best orbitals, the longest wave length transition is rather accurately given for butadiene by any level of configuration interaction treatment. The second transition is, however, considerably more sensitive to the completeness of the configuration interaction, and while the doubly excited treatment gives substantially the same results as the complete treatment, the singly excited treatment does not. (Unfortunately the $N \rightarrow V_2$ transition is forbidden and unobserved, so no comparison with experiment can be made on this point.) If poor wave functions are chosen initially, they are improved somewhat by the inclusion of singly excited configurations, and still more by the inclusion of the doubly excited configurations. The results show, however, that it is desirable to start with as good orbitals as one can obtain and to push the configuration interaction treatment as far as possible.

Returning again to Table V, for the dienes possessing a twofold axis of symmetry there is a clear differentiation between the first and second transitions, the first being strongly allowed and the second forbidden, regardless as to how far the configuration interaction treatment is carried. For the compounds which lack this twofold axis, the above situation continues to prevail at the level of the first excited treatment. However, when the diexcited configurations are included, a very strong mixing occurs of the two excited configurations corresponding to the two lowest energy transitions. There result two states somewhat different in energy, which are obtained by mixing similar amounts of the configuration to which a transition would be allowed with one to which it is forbidden. Experimentally, one might expect to see two absorption maxima with similar intensities, and the sum of the integrated areas of the two absorption bands should be comparable with that of the single band in butadiene. The two transitions generally come some 10 to 20 $m\mu$ apart, however, so that experimentally they may, but probably will not, be resolved. Since these absorption bands generally show a number of peaks due to the vibrational fine structure, it may or may not ever be possible to differentiate the two bands by inspection, so we have predicted that the spectrum will show one absorption maximum at the average wave length of the two calculated values.

Other Polyenes. 1,3-Cyclohexadiene provides a more stringent test of the calculation than does *trans*-butadiene, because the $N \rightarrow V_1$ and $N \rightarrow V_2$ transitions are predicted both to be strong and to be in the accessible region of the spectrum. Assuming the chromophoric system to be planar (which simplifies the calculations without introducing much error⁴), the transitions were calculated to lie at 5.10 and 6.64 e.v., respectively, including all singly excited configurations. When the doubly excited configurations were added, these values changed to 5.163 and 5.754 e.v. The experimental values reported²⁰ are 4.98 and 6.04 e.v., respectively, in reasonable agreement with the calculations.

Two additional conjugated systems were next studied

(20) E. P. Carr and H. Stucklen, *J. Chem. Phys.*, **6**, 55 (1938); see also footnote *g* in Table V.

in an effort to test further the limits of applicability of the method. Benzene and *s-trans,trans,s-trans*-1,3,5-hexatriene were examined, and the data are summarized in Table VII. For benzene the agreement for the $N \rightarrow V_1$ transition is good; the others are off by 0.2–0.6 e.v., depending on which experimental value is chosen for comparison. The maximum disagreement between the theoretical and experimental values occurs for the ${}^1B_{1u}$ transition, and amounts to 11–19 $m\mu$.

Table VII. Transition Energies of Benzene and 1,3,5-Hexatriene (e.v.)

Compound	Transition	Calcd.	Obsd.	Ref.
Benzene	${}^1B_{2u}$	4.82	4.79	<i>a, b</i>
			4.71	<i>c</i>
	${}^1B_{1u}$	5.65	6.19	<i>a</i>
			5.96	<i>c</i>
			6.10	<i>d</i>
	${}^1E_{1u}$	7.18	6.94	<i>a, d</i>
6.76			<i>c</i>	
Hexatriene	V_{34}	5.37 (strong)	5.14 (strong)	<i>e, f</i>
	V_{35}	5.32 (forbidden)	...	
	V_{36}	6.29 (very weak)	...	
	V_{25}	7.11 (weak)	7.11 (medium)	<i>f</i>
	V_{24}	7.21 (forbidden)	...	

^a H. B. Kelvins and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).
^b W. O. Robertson, S. E. Babb, Jr., and F. A. Matsen, *ibid.*, **26**, 367 (1957).
^c R. Pariser, *ibid.*, **24**, 250 (1956).
^d M. A. El Sayed, *ibid.*, **36**, 552 (1962).
^e See footnote *g* in Table V.
^f W. C. Price and A. D. Walsh, *Proc. Roy. Soc. (London)*, **A185**, 182 (1946).

A check was made to see if substitution of a methyl group on benzene to give toluene would lead to the red shift of the $N \rightarrow V_1$ transition which is known to occur experimentally. After the singly excited configuration interaction treatment, the $N \rightarrow V_1$ transitions are calculated to be at 5.15 and 5.07 e.v. for benzene and toluene, respectively, which is about the right difference. The $N \rightarrow V_1$ and $N \rightarrow V_2$ transitions are also calculated to be weakly allowed in toluene, consistent with experiment.

The results for hexatriene are satisfactory, and there seems to be little doubt but that the various geometric and conformational isomers of the hexatrienes could be accurately treated by the present method as far as the $N \rightarrow V_1$ transition. The $N \rightarrow V_1$ transitions for the trienes should now be accurately calculable by the present method including only singly excited configurations; thus the value calculated for the $N \rightarrow V_1$ transition ($V_0 \rightarrow V_{34}$) for hexatriene is 5.26 e.v. if only singly excited states are included, while it is 5.37 e.v. when the doubly excited states are included. The $N \rightarrow V_2$ transition is forbidden and unobserved. The allowed $N \rightarrow V_3$ and $N \rightarrow V_4$ transitions are, after inclusion of the singly excited configuration interactions, predicted at 6.77 and 9.88 e.v., with oscillator strengths of 0.05 and 0.14, respectively. Configuration interaction with the doubly excited configurations probably does not change the oscillator strengths very much, but it lowers their energies to 6.29 and 7.11 e.v., respectively. Experimentally, there is absorption of moderate strength centered at 7.11 e.v. which earlier workers²¹ considered to be a Rydberg transition, but its assignment as the $N \rightarrow V_4$ transition would not

(21) See footnote *f*, Table VII.

be inconsistent with the known facts. Whether or not the changes in the higher energy transitions which result from inclusion of the doubly excited configurations can be called improvements will require further experimental data for comparison.

As an additional type of system, we wished to treat some nonconjugated hydrocarbons and chose norbornadiene and barrelene as representative examples. Cyclopentadiene was also examined. There is some ambiguity here, since the substituents on the olefinic carbons are not alkyl groups, but rather allyl groups, and their inductive effects would be somewhere between those of a methyl and of a carbon atom. Having no way to estimate just where between these limits the actual value would lie, we have done the calculation for the two limiting cases. The experimental values for the bicyclic compounds lie between the calculated limits (Table VIII) and could be fit by

Table VIII. Calculated and Observed Transitions of Norbornadiene, Barrelene, and Cyclopentadiene (e.v.)

Compound	Transition	Calcd. ^a	Calcd. ^b	Obsd.	Ref.
Norbornadiene	N → V ₁	5.29	6.08	5.87	<i>c</i>
	N → V ₂	6.81	7.59	≥6.59	
Barrelene	N → V ₁	5.01	...	5.54 ^d	<i>e</i>
	N → V ₂	6.34	...	6.27 ^d	
Cyclopentadiene	N → V ₁	4.53	4.96	5.29	<i>f</i>
	N → V ₂	5.39	5.71	6.16	<i>f</i>

^a Z_C of C_π orbitals being 3.002 (treating the substituents as methyl groups). ^b Z_C of C_π orbitals being 3.183 (treating the substituents as carbon atoms). ^c R. B. Hermann, *J. Org. Chem.*, **27**, 441 (1962). ^d Corrected to gas phase. ^e H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960). ^f Present investigation.

using an inductive parameter for the allyl group. We have not done this because it is not now certain whether or not it would be meaningful. There are other difficulties to be considered with these compounds, of which the following appear to be potentially important: the systems are not coplanar, and σ - π interactions may not be negligible; the compatibility of the Mulliken relationship with σ - and π -overlaps in the present context is uncertain; and strain on the σ -system is present in certain of these compounds and its effect on the π -system is uncertain. The last mentioned of these difficulties and the inductive effect of the allyl group are both possible contributors to the failure of the calculations to predict adequately the cyclopentadiene spectrum (Table VIII). The latter molecule is a rather special case which will have to be studied further.

Singlet-Triplet Transitions. Finally, the triplet states for some of these molecules were considered as their energies were not well predicted earlier.⁴ For the triplet states the configuration interaction treatment was limited to singly excited configurations. The results are excellent for the $N \rightarrow T_1$ transitions (Table IX),

Table IX. Observed and Calculated Triplet Transitions (e.v.)

Compound	Transition	Calcd.	Obsd.	Ref.
<i>trans</i> -Butadiene	N → T ₁	3.00	3.2	<i>a</i>
	N → T ₂	4.55	3.9	<i>a</i>
<i>cis</i> -Butadiene	N → T ₁	2.84	2.9	<i>b</i>
	N → T ₂	4.49	...	
1,3-Cyclohexadiene	N → T ₁	2.48	2.9	<i>a</i>
	N → T ₂	4.25
1,3,5- <i>trans</i> -Hexatriene	N → T ₁	2.48	2.6	<i>a</i>
	N → T ₂	3.93	3.2	<i>a</i>
Ethylene	N → T ₁	4.43	4.6	<i>a</i>
	N → T ₂	3.81	3.76	<i>c</i>

^a D. F. Evans, *J. Chem. Soc.*, 1735 (1960). ^b Estimated from data in footnote *d*, Table VII. ^c D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

but the agreement with the limited experimental data for $N \rightarrow T_2$ transitions is not very good, similar to the results with the singlet transitions when the doubly excited configurations were omitted from the treatment. It is noted that the $N \rightarrow T_1$ transition for *cis*-butadiene is predicted to be at a longer wave length than that of the *trans* by some 23 m μ , which is reasonably consistent with Hammond's experimental work.²²

The treatment described herein has been and is currently being extended to systems containing other first row elements, and these extensions will be described in due course. It is of interest to note here that while the replacement of a hydrogen by a methyl in hydrocarbon systems invariably leads to a shift of the $N \rightarrow V_1$ transition to longer wave length, the identical procedure when applied to carbonyl compounds predicts that as one goes from formaldehyde to acetaldehyde to acetone, the $n \rightarrow \pi^*$ transitions are calculated to move systematically to shorter wave length, in quantitative agreement with experiment. The effect of alkyl substitution on unsaturated ketones is much larger than on olefins (10–18 m μ vs. 5 m μ), so the ability to calculate accurately the absorption maxima in ketones will be a much more stringent test of the method than that described herein.

(22) G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963).