Organic Quantum Chemistry. XIX. Calculation of the Electronic Spectra of Unsaturated Ketones[1,2]

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Abstract: The ultraviolet spectra of a number of saturated and unsaturated aldehydes and ketones having various types of alkyl substitution patterns have been calculated using a modified Pariser–Parr method which allows for the inductive effect of the alkyl groups by a variable electronegativity approach. All singly and doubly excited configurations are included in the configuration interaction treatment. The agreement with experiment for $\pi \rightarrow \pi^*$ transitions is good, but various problems are encountered and discussed with $n \rightarrow \pi^*$ excitations.

The calculation of the ultraviolet spectra of ketones has received relatively little consideration in the literature. Only formaldehyde has been the object of a reasonably complete investigation, which utilized the core and peel method of Parks and Parr.[3] Sidman[4] also considered this molecule and benzoquinone in a Pariser–Parr–Pople type of calculation. Nishimoto and Forster[5] studied the π system of benzoquinone, and Julg, Bery, and Bonnet[6] carried out an SCF treatment of this molecule, and then included the lone-pair electrons at the end. Both of these molecules have been studied by Anno and coworkers.[7,8] But other examples of this class of compounds have only been the object of neglect.

Using the basic antisymmetrized molecular orbitals procedure with configuration interaction (ASMO–CI) as developed by Pariser and Parr,[9] and as extended by the variable electronegativity self-consistent field (VESCF) method of Brown and Heffernan,[10] we have calculated the spectra of formaldehyde, acetaldehyde, acetone, and a series of methylated unsaturated aldehydes and ketones. In a previous paper,[11] a description of the modifications of the basic method necessary for the consideration of alkyl-substituted compounds was given, and in a subsequent extension[12] of this original work to a representative selection of many different types of unsaturated hydrocarbons, amendments were introduced with respect to the empirical determination of β in the $\mathbf{H}_{\text{CORE}}$ matrix, a shift to SCF orbitals was made, and penetration effects were included in a more complete way.

Thus the ground work laid by this earlier study, and its success with a wide variety of hydrocarbons, leaves necessary only a determination of the properties of the two atomic orbitals on oxygen before the calculation of electronic spectra of ketones can be carried out. Specifically we must consider two independent variables: the internuclear distance (R) between carbon and oxygen, and the effective nuclear charge (Z) for an oxygen orbital; and then four quantities which are dependent on R and/or Z. They are: ionization potential (I), resonance integral (β) between oxygen and carbon p orbitals, the one-center atomic coulomb repulsion integral for oxygen (γ_{OO}), and the atomic exchange-repulsion integral ($\chi_{\text{O}_n\text{O}_\pi}$). In addition one must consider whether or not the π orbital of oxygen and the n orbital are to be treated identically. Each of these problems are considered below in detail.

Method of Calculation

First we shall develop the basis for the calculation of the dependent parameters, as this constitutes simply a logical extension from the earlier work[11,12] from carbon to oxygen orbitals.

The Interdependence of Ionization Potential and Nuclear Charge. Assuming for the moment that Z for an orbital on an atom is available, it is necessary to know the dependence of I on Z. The equation relating these two quantities was therefore developed both for the π orbital (O_π) and the n orbital (O_n) on oxygen in just the same manner as was used earlier for carbon. Specifically, since the ionization potential is directly proportional to the nuclear charge to a good approximation, then for the same effective orbital charge Z, the ionization potential of an oxygen-like orbital (I_O) may be determined from the ionization potential of an isoelectronic atom (I_X), together with the ratio of the nuclear charges, N_O and N_X.

$$I_\text{O} = I_\text{X}(N_\text{O}/N_\text{X})$$

In Table I this equation is applied to the experimental ionization potentials (I_X)[13] for a number of isoelectronic

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[1] Paper XVIII: T. W. Stuart and N. L. Allinger, *Theoret. Chim. Acta*, in press.

[2] This research was supported by Grant GP 4290 from the National Science Foundation.

[3] J. M. Parks and R. G. Parr, *J. Chem. Phys.*, **32**, 1657 (1960); see also T. Anno and A. Sado, *ibid.*, **26**, 1759 (1957).

[4] J. W. Sidman, *ibid.*, **27**, 429 (1957).

[5] K. Nishimoto and L. S. Forster, *Theoret. Chim. Acta*, **4**, 155 (1966).

[6] A. Julg, J. C. Bery, and M. Bonnet, *Tetrahedron*, **20**, 2237 (1964).

[7] T. Anno, A. Sado, and I. Matubara, *J. Chem. Phys.*, **26**, 967 (1957).

[8] T. Anno and A. Sado, *ibid.*, **26**, 1759 (1957).

[9] R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953).

[10] R. D. Brown and M. Heffernan, *Australian J. Chem.*, **12**, 319 (1959).

[11] N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **87**, 2081 (1965).

[12] N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theoret. Chim. Acta*, **8**, 101 (1967).

Table I

	Z	I_X	I_O
	$O_\pi(s^2{}_{x^2y^2} \rightarrow s^2{}_{x^2y})$		
$N^- \rightarrow N$	3.55	2.60	3.12
$O \rightarrow O^+$	4.55	17.21	17.21
$F^+ \div F^{2+}$	5.55	35.18	30.15
	$O_n(s^2{}_{x^2y^2} \rightarrow s^2{}_{xyz})$		
$N^- \rightarrow N$	3.55	0.86	1.03
$O \rightarrow O^+$	4.55	14.75	14.75
$F^+ \rightarrow F^{2+}$	5.55	32.03	27.45

ionizations. (The nuclear charges are calculated assuming inclusion of 1s electrons in the core.) The variation of I_O with Z may then be found by deriving a parabolic equation to describe the dependence, and eq 1 and 2 result.

$$I_{O_\pi} = -0.575Z^2 + 18.748Z - 56.187 \qquad (1)$$

$$I_{O_n} = -0.511Z^2 + 17.857Z - 55.925 \qquad (2)$$

The use of the first rather than the second ionization potential for the nonbonding orbital might be questioned; however, we can see no particular advantage to either approach, and have followed the treatment of Anno.[14] Likewise, the core integral α is obtained for the n orbital by adding the one-center coulomb repulsion integral, but we also include penetration integrals as discussed earlier.[12]

The Resonance Integrals. The core integrals (β) for nearest neighbors are calculated from the Mulliken formula

$$\beta_{pq} = -AS_{pq}(W_p + W_q)/2(1 + S_{pq}) \qquad (3)$$

where A is determined by the empirically chosen reference set of resonance, overlap (S), and ionization integrals.[12] Though the effect of choosing a new reference A for the carbonyl bond was investigated, the change required to produce the best fit with experiment was too small to justify the programming involved. The value for A, then, was the same as used for the all-carbon compounds: 1.1863 eV. In eq 3 the quantity $S_{pq}/(1 + S_{pq})$ is replaced by an empirical expression for internuclear distances larger than those for nearest neighbors. Specifically, the following expression was employed when the overlap integral S was less than 0.14.

$$\beta_{pq} = -[A(W_p + W_q)/2](44095S^5 - 15084S^4 + 1785S^2 - 80.4S^2 + 1.60S)$$

This expression allows β to fall off somewhat more rapidly as noted earlier.[12] The inclusion of nonneighboring resonance integrals has been discussed recently by Flurry and Bell.[15] Generally, the quantity W in eq 3 is just the ionization potential, but in the case of nonplanar ketones where the overlap integral is nonzero between the carbon and the nonbonding orbitals on oxygen, the resonance integral would be required to take account of the number of electrons in the n orbital.

$$W_n = I_n + \gamma_{nn}$$

Coulomb Repulsion Integrals. The one-center coulomb integrals, γ_{pp}, were taken from the spectroscopic ionization potential and electron affinity.

$$(\pi_o\pi_o/\pi_o\pi_o) = (n_on_o/n_on_o) = 14.52 \text{ eV}$$

Since the theoretical repulsion integrals are proportional to the effective charge, Z, and this valence-state integral corresponds to a Slater charge, the calculation for any particular orbital is simply

$$\gamma_{pp} = 14.52(Z_p/Z_{\text{Slater}}) \text{ eV}$$

Two-center integrals are scaled down from theoretical values as described earlier.[11]

The special case of the one-center, two-orbital integral $(\pi_o\pi_o/n_on_o)$ is solved by an adaptation of an expression given by Anno.[14] For our problem the value depends on the one-orbital coulomb integrals of the π and n orbitals (which have different charges; see below) and the two-orbital exchange integral which is described immediately.

$$\gamma_{\pi n} = {}^1\!/_2(\gamma_\pi + \gamma_n) - 2\chi_\pi$$

For a Slater Z, the value is 12.8242 eV.

Exchange Repulsion Integrals. In our initial investigation into the spectra of ketones, we sought to continue the complete neglect of differential overlap. However, its exclusion in this situation of two orbitals on the same center is no longer warranted. For orbitals on different centers, the magnitude of the atomic exchange integral, χ, is approximately 0.1 eV; here it is of the order 0.8–0.9 eV. The experimental value is determined from the Slater–Condon parameter G_2,[16] which is equal to 0.2826 eV.[13]

$$(\pi_on_o/\pi_on_o) = 3G_2$$

The exchange integral for two specific orbitals was then found in a manner identical with that used for the one-center coulomb integral.

$$\chi_{\pi n} = 0.8479[{}^1\!/_2(Z_\pi + Z_n)/4.55]$$

Bond Lengths. For carbon–carbon bonds we use the bond order–bond length relationship derived by Dewar and Schmeising;[17] the resulting bond lengths are self-consistent to within 0.002 Å. For the ketone bonds we developed an analogous equation, but it was discovered that all carbon–oxygen π bond orders were so similar (between 0.92 and 0.94) that it appeared to introduce an unnecessary complexity, so we employed an experimental acetaldehyde bond length,[18] 1.216 Å, for all compounds. All bond angles were assumed to be 120°.

Effective Nuclear Charges. The choice of initial shielding constants for variously substituted carbon atoms has been described previously,[11] and we use identical values here. For the oxygen π orbital, the Slater charge, 4.55, is the most reasonable and consistent assignment. The n orbital presents a more complex situation.

On first consideration one might also assign the Slater charge to the n orbital of oxygen. Consider, then, the

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

[14] T. Anno, *J. Chem. Phys.*, **29**, 1161 (1958).

[15] R. L. Flurry and J. J. Bell, *J. Am. Chem. Soc.*, **89**, 525 (1967).

[16] R. S. Mulliken, *J. Chem. Phys.*, **1**, 782 (1934).

[17] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

[18] L. C. Krisher and E. B. Wilson, Jr., *J. Chem. Phys.*, **31**, 882 (1959).

orbitals resulting from the VESCF treatment. A shift of electron density from the carbon to oxygen orbital directs an expansion of the latter, and a consequent decrease from the initial Slater charge. However, the n orbital does not change. This approach is inconsistent with the physical model associated with the Slater effective charge—that it is an identical property for any similar orbitals on the atom, dependent only upon the nucleus and core electrons. From this physical picture both p orbitals should exhibit the same shielding constant. On the other hand, within the VESCF method, this physical concept of a Slater orbital may be considered inappropriate: the orbital exponent may be thought of as simply a mathematical parameter which may be varied to minimize the energy of the system. Furthermore, comparison with the experimental n → π^* transitions leads to conclusive persuasion in the inadequacy of the Slater charge for the n orbital.

What we should really like to know is the value for the n orbital exponent which minimizes the energy of the molecule, or, to a first approximation, the energy of the σ system. In order to obtain this value, one would need the energies of the σ orbitals. We were not willing to undertake this determination, and hence employed an empirical approach.

Two ways of fitting the experimental data might be used. First, one could vary the hybridization of the n orbital. This means of attacking the problem is fairly extensive in its ramifications and we are pursuing it separately. Another method would be to simply choose an orbital exponent for the pure p orbital we have considered heretofore. The choice of an exponent was based upon the experimental n → π^* transitions of acetone and cyclohexanone.[19] The required value for Z to give an intermediate fit for both saturated ketones was 4.471. A number of compounds were studied, and it was found that, in general, the larger the system treated, the greater the deviation from experiment observed.[20] By this method we predict a much longer wavelength transition for a dienone, for example, than is actually observed.

In other words, as the energy of the π^* molecular orbital is lowered—in the series ketone, enone, dienone—so too must the n orbital move to a lower energy level if we are to agree with experiment. This might lead one to consider the chaining together of the two oxygen atomic orbitals. Though the variation of the n orbital along with the π-orbital charge is, at best, a somewhat dubious approach from a theoretical standpoint, it has additionally one obvious defect in that charge will not be conserved. With each successive iteration during the SCF procedure, the total electron density (summed over all the centers) will be reduced. This defect can be overcome, however, as can be shown by taking acetone as an example. If the charge on carbon increases by a small amount (ΔZ_C) in an iteration, then the change at each oxygen may be calculated so as to conserve charge.

$$\Delta Z_O = -{}^1/_2\Delta Z_C \qquad (4)$$

Now whereas in the first approach mentioned above (with a constant Slater charge for the n orbital) the transition was predicted to fall at a position approximately 1 eV too blue, the experimental comparison in this second case gave a calculated value which was about 1 eV too red. The restraint placed upon the process of minimizing the energy of the system by the use of eq 4 is therefore undesirable. Surprisingly, however, it has no appreciable effect on the $\pi \rightarrow \pi^*$ transition.

Surveying the last two attempts, it can be seen that experiment required results in between the pair. Accordingly, the fourth empirical method combines aspects of both preceding approaches. We remove the restriction described by eq 4, but still vary the n orbital slightly.

Returning to the second attempt, where an n orbital of charge 4.471 was used to fit acetone and cyclohexanone, it was found that the final charge on the oxygen π orbital was 4.388 after the VESCF treatment. The difference is thus 0.083. This relationship between the two orbitals of acetone was chosen as the basis for any two ketone oxygen orbitals.

$$Z_n = Z_\pi + 0.083 \qquad (5)$$

In essence, one allows the π system to reach equilibrium, and then, on the next SCF iteration, supplies the charge for the n orbital. Another iteration is seldom necessary for, as noted above, the shielding constant of the n orbital has little influence on the π system.

In the case of nonplanar molecules, the situation is complicated by the interaction of the n orbital with carbon orbitals. Here we simply set the initial charge equal to that found in the isomeric planar compound and then proceed with a VESCF treatment of the whole system. One might assume or expect a serious breakdown of the method here, since if the interaction with the system were strong, there would be a redistribution of charge, and one would no longer be dealing with lone-pair electrons, but just another p orbital in the π system. This situation does not occur, however, because any carbon orbital which is not orthogonal to the n orbital is at least 3 Å distant. Hence, the electron density is still very close to 2, and we still have essentially two lone-pair electrons.

One fault explicit with eq 5 is that it does not conserve charge in the system, but we were forced to conclude that, in order to do this one might very well need to treat the entire σ system. For a simple, predictive model, the approach described is the best of the several alternatives, in spite of its theoretical shortcomings.

Configuration Interaction. All singly and doubly excited configurations were included in the determination of the final wave functions and states. Koutecký, Hlavatý, and Hochman[21] and Allinger and Stuart[22] have discussed the extent of configuration interaction recently and concluded that this is probably the minimum amount which can be expected to give results of predictive value to the experimentalist.

Extinction Coefficients. Calculated values for the oscillator strengths were converted to extinction coefficients by the equation $\epsilon = 41{,}700f$ (based on a fit to ethylene) as discussed earlier.[12]

Results and Discussion

The calculated and experimental values for the ketones studied are summarized in Table II. The ex-

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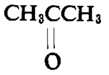
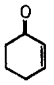
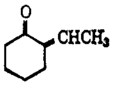
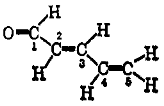
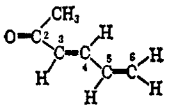
(19) Gas-phase spectra, present investigation.

(20) L. W. Chow, Ph.D. Thesis, Wayne State University, 1967.

(21) J. Koutecký, K. Hlavatý, and P. Hochman, *Theoret. Chim. Acta*, 3, 341 (1965).

(22) N. L. Allinger and T. W. Stuart, *J. Chem. Phys.*, 47, 4611 (1967).

Table II

No.	Parent	Methyl substitution	Calcd			Exptl		
			eV	mμ	ε	mμ	ε	Ref
1	$H_2C{=}O$	...	3.92	316	0	310		*a*
			7.76	160	13,900	156		*b*
2	$CH_3CH{=}O$	...	4.09	304	0	294		*c*
			7.54	164	13,300	160		26
3	 $CH_3\overset{\underset{\|}{}}{}C(=O)CH_3$	...	4.38	283	0	275		19
			7.41	168	12,900	157	20,000	26
4		...	3.74	331	0	324–344		29
			5.88	211	28,900	216	11,200	*d*
			6.27	198	600			
5		2	3.75	331	0	337	14	29
			5.64	220	23,600	227	9,100	*e*
			6.10	203	5,000			
6		3	3.76	329	0	334–350		29
			5.69	218	28,100	222	15,000	*d*
			6.22	199	600			
7		2,3	3.76	330	0	322–342		29
			5.47	227	25,000	232	13,200	*d*
			5.99	207	2,900			
8		...	3.66	339	0	324–329		29
			5.01	248	9,300	237	7,400	*d*
			5.99	207	900			
9		...	3.67	338	0	325	51	*f*
			4.93	252	18,700	248	27,800	*f*
			5.36	231	23,900			
10		2	3.68	337	0			
			4.66	266	18,400			
			5.36	231	21,900			
11		3	3.67	338	0			
			5.03	247	19,800			
			5.14	241	22,200			
12		4	3.65	340	0			
			4.66	266	18,000			
			5.37	231	22,600			
13		5	3.66	339	0			
			4.78	259	22,900	261	32,000	*f*
			5.25	236	18,900			
14		5,5	3.65	340	0			
			4.66	266	26,500	275	30,000	*g*
			5.16	240	14,600			
15		...	3.82	325	0			
			5.11	243	22,400			
			5.37	231	20,700			
16		3	3.85	322	0			
			4.88	254	20,000			
			5.38	230	21,800			
17		4	3.83	324	0			
			5.15	241	34,000			
			5.24	237	9,000			
18		5	3.81	326	0			
			4.83	257	20,000			
			5.40	230	20,400			
19		6	3.82	325	0	335–350	100	*h*
			4.95	250	28,200	263	20,000	*h*
			5.28	235	14,300			
20		6,6	3.81	325	0			
			4.82	257	32,000			
			5.21	238	9,800			

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[a] A. D. Cohen and C. Reid, *J. Chem. Phys.*, **24**, 85 (1956). Measured in isopentane. [b] G. Fleming, M. M. Anderson, A. J. Harrison, and L. W. Picket, *ibid.*, **30**, 351 (1959). [c] K. Bowden, E. A. Braude, and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946). Measured in hexane. [d] R. Mecke and K. Nozck, *Chem. Ber.*, **93**, 210 (1960). [e] W. W. Rinne, H. R. Deutsch, M. I. Bowman, and I. B. Joffe, *J. Am. Chem. Soc.*, **72**, 5759 (1950). [f] E. L. Pippen and M. Nonaka, *J. Org. Chem.*, **23**, 1580 (1958). [g] I. N. Nazarov and Zh. A. Krasnia, *Zh. Obshch. Khim.*, **28**, 2440 (1958); *J. Gen. Chem. USSR*, **28**, 2477 (1958). [h] P. Grammaticakis, *Bull. Soc. Chim. France*, 865 (1953).

perimental $\pi \rightarrow \pi^*$ transitions which were determined in solvents have been corrected to the vapor phase as described earlier for the alkenes[12] by the method of Bayliss.[23] For the $n \rightarrow \pi^*$ transitions the corrections are negligible. A characteristic blue shift of the $n \rightarrow \pi^*$ bands in more polar solvents has been documented,[24] and this has been attributed to hydrogen bonding, with lesser contributions from the dielectric effect, in the work of Hayes and Timmons.[25] However, the shift is not very large in any case, and for the cyclohexenones which were all measured in hexane or cyclohexane, the shift involved with the change to the vapor phase is expected to be negligible. This might not be the situation for the dienones where the spectra were taken in alcohol, but here the band is quite broad and overlaps the $\pi \rightarrow \pi^*$ transition, making a realistic analysis extremely difficult. First, we shall discuss the $\pi \rightarrow \pi^*$ transitions and then the transitions from the nonbonding orbital.

$\pi \rightarrow \pi^*$. The compounds of the series formaldehyde, acetaldehyde, acetone are experimentally observed to have $\pi \rightarrow \pi^*$ transitions close to 160 mμ, but there is considerable uncertainty here. The $\pi \rightarrow \pi^*$ transition of acetone does not appear to have ever been assigned, although it has been discussed.[26] The absorption near 190 mμ in acetone does not have a sufficient oscillator strength to be the sought-for transition, which therefore probably occurs near 160 mμ. The extensive absorption[26] in this region, which is expected to involve the σ system also,[26,27] together with experimental difficulties led to an inconclusive assignment. Our best guess is that the $\pi \rightarrow \pi^*$ absorption occurs at 157 ± 10 mμ. Our calculated value for the transition is at a wavelength which may be too long, but which is acceptable in view of the experimental uncertainties.

The value for the resonance integral β for the carbonyl bond was determined by a straightforward application of the Mulliken formula using the hydrocarbon data described earlier.[11,12] We prefer not to introduce any additional parameters unless it is clear that they will lead to a significant improvement. Actually, after the calculations were complete it became clear that the calculated wavelengths are systematically a few millimicrons too blue. This systematic error could be removed by assuming the C=O bond length was slightly (about 0.002 Å) larger than the value used, but it was not regarded as worthwhile to repeat the calculations for this small change.

Compounds **2–5** are in very good agreement with experiment. Three of these ketones have calculated transitions which are 4–5 mμ lower than the observed value, being well within experimental error. The slightly larger discrepancy, 7 mμ, with 2-methylcyclohexenone is attributable to a smaller correction to the gas phase resulting from an abnormally low reported extinction coefficient. The experimental value of the latter may be inaccurate, as the syntheses of the compound reported are such that one would expect some contamination by the unconjugated (Δ^3) isomer. A slightly larger shift is predicted for α than for β substitution, in contradiction to Woodward's rules,[28] but in agreement with experiment for these particular compounds. In dimethylcyclohexenone the shifts are found to be additive.

Compound **6** is, as far as the chromophore is concerned, the *s-cis* geometric isomer of 2-methylcyclohexenone. A red shift of 28 mμ relative to that compound is calculated and, together with the reduced value for the oscillator strength, is typical of the relationship usually experimentally observed for *s-cis* and *s-trans* conformers. This shift may be compared with an experimental shift of only 10 mμ. The difference indicates the compound is not completely planar. In principle it should be possible to calculate the degree of nonplanarity from the observed shift, although we have not carried out the calculation. The calculated extinction coefficient may be seen to have dropped relative to that of the *s-trans*, in agreement with the analogous situation for *s-trans*-butadiene and 1,3-cyclohexadiene. The experimental ϵ has not decreased to the same extent, which again throws into doubt the measured extinction coefficient of 2-methylcyclohexenone.

The calculated spectra of the dienones showed an unexpected feature. Here we have predicted in each case two strong transitions separated by from 6 to 35 mμ. (A third very weak $\pi \rightarrow \pi^*$ transition is also calculated, usually at about 200 mμ.) Though it is not reported whether any of the four compounds for which experimental values are available are in the *s-cis* or *s-trans* conformation, the agreement with the $\pi \rightarrow \pi^*$ transitions of lowest energy calculated for the expected *s-trans* conformers is reasonably good. On the other hand, this comparison is not strictly legitimate since these are calculated to show two strong absorption bands. Hence, we have plotted the calculated ultraviolet spectra with the aid of a program described earlier.[29] Except for two cases, the plotted calculated spectra of the aldehydes and ketones gave one peak approximately centered between the two $\pi \rightarrow \pi^*$ transitions and with an extinction coefficient 30–35,000. The two exceptions were 2-methylpentadienal and 4-methylpentadienal. Here the two bands shifted 2–4 mμ toward each other with little change in intensity.

Despite the diverse nature of the tabular forms of the initially calculated spectra, these resultant graphs showed a systematic 5–6-mμ red shift per methyl group, and only a 1- or 2-mμ difference between α, β, γ, and δ positions of methyl substitution. This is in contrast to the usually observed 10-, 12-, and 18-mμ shifts with α, β, and γ substitution in steroids.[28]

The shifts tend to be somewhat larger in solvents (as usually measured) because the same energy difference corresponds to a larger number of millimicrons at longer wavelengths. Still, it would seem that our calculated shifts are on the low side for α- and β-substituted double bonds, but the really conspicuous differences between our calculated values and those predicted by Woodward's rules are in the γ- and δ-substituted compounds. The validity of the 18-mμ value utilized by Woodward's rules is based on rather meager experimental data, however.[28]

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(28) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959.

(29) N. L. Allinger, *Tetrahedron*, **22**, 1367 (1966).

Thus, we must consider the possible causes for the disagreement with experiment. First, the extinction coefficients might be inaccurate, either by calculation alone or in comparison with experiment. Though theoretical calculations of ϵ are often only correct to an order of magnitude, even if one of the values were zero here, we would still have to contend with an apparently random behavior of the remaining allowed $\pi \rightarrow \pi^*$ transition. Looking at Table II, one can note that neither the lower nor the higher $\pi \rightarrow \pi^*$ transition shows any obvious logical progression, whereas the average of the two transitions exhibits a comparatively consistent development. Furthermore, drawing from our results with other π systems, such an inaccuracy does not seem tenable. By saying "in comparison with experiment" as a source for the discrepancy, it is meant that the experimental situation is not advantageous. Even if our calculated extinction coefficients were only slightly in error relative to one another, all of the transitions in the plotted spectra would be merged. Experimentally, this would be nearly insuperable with the difficulties of obtaining pure specimens of the compounds studied here. Too, in the case of aliphatic compounds, a side band might be attributed to rotational isomerism. Although this possibility could not be considered for an analogous steroidal system, it would be reasonable for a worker to suspect a strong vibrational transition, since the majority of dienones only possess one observable band and the literature is unanimous on this point.

If then we conclude that there really are two bands in the ultraviolet, heretofore unrecognized, then we need only postulate that it is simply in the magnitude of the contribution of a methyl group to the original p-orbital charges in which we err (for with a small change all the plotted transitions would shift into experimental agreement). Looking back to our earlier work,[12] there is some evidence for this, for example, with the methylazulenes where the direction of the shifts caused by substitution of a methyl group on azulene is always predicted correctly, but where the magnitude is again in error.

It would thus be interesting to see whether these two peaks could be resolved experimentally. Aside from the usual difficulties with such determinations, these two bands present an additional obstacle. Inspection of the eigenvectors of the two states shows the major contribution arises from the configuration resulting from a transition from the highest filled to the lowest unfilled orbital in both cases. Hence, both are likely to shift similarly with a change in solvent, temperature, or pressure, precluding any easy resolution of the problem. Our work here, however, would indicate that compounds **8** and **10** are the more likely to be useful of those considered.

The experimental data on the compounds formaldehyde, acetaldehyde, acetone indicate a substantial blue shift upon alkylation, which is the reverse of that found for transitions of the $\pi \rightarrow \pi^*$ type. Our calculated values reproduce these differences rather well, which suggests that the differences (as opposed to the absolute values) are adequately handled by the theoretical treatment.

For the unsaturated compounds the situation is less simple. For these compounds, the $n \rightarrow \pi^*$ transition has not been exhaustively studied experimentally because it is not particularly helpful for characterization, although it has been claimed[30] that the position of absorption is affected in a predictable manner by substitution. Another difficulty is that the $n \rightarrow \pi^*$ absorption is often submerged in the intense $\pi \rightarrow \pi^*$ absorption, and it may be difficult to assign a band position to the former. Table II shows the available data. The ranges reported result from determinations on from 3 to 12 cyclic molecules—mostly steroids—incorporating an enone submoiety. With most of the compounds a fine structure of five or six lines was observed. In accordance with our earlier work we choose the line closest to the center of the integrated absorption intensity, for it is the Franck-Condon band and not the (0,0) line which we wish to predict.

Cookson and Dandegaonker interpret their data as indicative of an approximately 6-mμ shift for each alkyl substituent on the olefinic bond.[30] It should be noted, however, that many of their compounds possess additional carbonyl groups which may well have small effects on the spectrum. As shown in Table II, we calculate no substitution effect on the $n \rightarrow \pi^*$ transitions, nor did we observe it with any of the alternate approaches to the treatment of the nonbonding orbital, as described above, in the n-orbital discussion.

With respect to the dienones, there are only reports for two of the compounds in the literature. The experimental data for compound **19** (hepta-3,5-dien-2-one) are instructive. It is one of the few unsaturated ketones for which a complete published spectrum exists. In ethanol, the $n \rightarrow \pi^*$ transition is completely buried by the $\pi \rightarrow \pi^*$ band, and in cyclohexane, there is still a considerable range, as indicated in Table II, within which the band center might fall. Thus, comparison of the $n \rightarrow \pi^*$ transition with experiment is, for the dienones, not really possible.

In summary, we feel that the reliable prediction of the $n \rightarrow \pi^*$ transitions requires considerable more study, experimental as well as theoretical. It seems probable that accurate prediction of these transitions will require explicit inclusion of the σ system, which has recently become feasible by means of semiempirical methods.[31] The $\pi \rightarrow \pi^*$ transitions appear to be reasonably well predicted, but there are a few problems here also.

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Appendix

Description of the Program. The following description is a brief outline of the calculations involved. For specifics one may refer to the treatise by Parr,[32] the dissertation by Miller,[33] and earlier papers.[11,12]

The program calculates the transition energies and oscillator strengths using a modified version of the Pariser-Parr-Pople[9,34] method. Essentially, the procedure consists of but three steps: the calculation of

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[30] R. C. Cookson and S. H. Dandegaonker, *J. Chem. Soc.*, 1651 (1955).

[31] For example, M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967); J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967).

[32] R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963.

[33] M. A. Miller, Ph.D. Dissertation, Wayne State University, 1963.

[34] J. A. Pople, *Proc. Phys. Soc.* (London), **A68**, 81 (1955).

molecular wave functions through a variable electronegativity self-consistent field (VESCF) treatment[10] of the atomic orbitals, then the use of a linear combination of these orbitals (LCAO) to build the ground and excited configuration wave equations, which are finally solved to give the state energies and orbitals. The transitions then result directly from the differences between the energies, and the oscillator strengths are derived from the orbitals.

The LCAO–VESCF orbitals are obtained from the diagonalization of a Hartree–Fock SCF matrix by an iterative procedure, which minimizes the energy of the ground state (V_0).

All computations were carried out on an IBM 7074 computer. For the largest molecules studied, seven atomic orbitals are used. They lead to a configuration interaction matrix of order 91 which is always factored as much as possible before diagonalization. The total computation time for such a molecule is about 20 min.

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p*K*'s of 1,1-Dinitro Compounds and Conformations of Dinitrocarbanions

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Abstract: p*K*'s in the series $RC(NO_2)_2H$ are related to inductive effects of nonconjugating substituents R through the expression, $pK = 5.24–3.60\sigma^*$. Acidities in this series are highly dependent on the steric requirements of R. Rationales for deviations of individual dinitro compounds from the $\rho^*–\sigma^*$ relationship are based on changing conformations in the conjugate dinitrocarbanions.

Most of the existing information regarding p*K*'s of 1,1-dinitroalkanes, $RC(NO_2)_2H$, has been reported in a series of papers by Novikov and coworkers.[1–4] In the course of a continuing study of how substituents affect properties and reactivities of dinitrocarbanions,[5–8] we have had occasion to repeat some of these measurements and to determine the ionization constants of a number of additional 1,1-dinitro compounds. Although our p*K* values for specific materials (dinitromethane and 1,1-dinitroethane) agreed well with data reported by the earlier investigators, we have arrived at somewhat different conclusions regarding the magnitude of substituent effects in this series.

In their most recent communication on the subject,[4] the earlier workers had suggested that dissociation constants of $RC(NO_2)_2H$ were related to Taft's σ^* values[9] of nonconjugated substituents R through the expression

$$pK = 5.22 - 1.74\sigma^* \qquad (1)$$

Of the 14 compounds cited (I, II, IIIa–d, IVa–d, V–VII, and XVIII of Table I), measured p*K*'s for 11 differed by less than 0.2 p*K* unit from predictions by eq 1, and arguments based on both steric and electronic considerations were enlisted to account for the "dropout" of the other three (VI, VII, and XVIII).

We have found, however, that in the cases of three additional p*K*'s reported by Novikov and coworkers for which the σ^*'s of R are now known or can be inferred[10] (VIII–X) and for seven p*K*'s determined in the present investigation (XI–XVII), eq 1 gives poor to unacceptable agreement with measured values. These experimental p*K*'s and the corresponding Δ's ($\Delta = pK_{\text{found}} - pK_{\text{calcd}}$) are assembled in Table I together with the earlier data.

We have applied standard least-squares treatments[11] (discussed in detail in the Appendix) to the data in Table I, appropriately weighted, to arrive at the following equation relating p*K*'s of $RC(NO_2)_2H$ compounds (unbranched in the 2 position, see below) to σ^* values of nonconjugating R's:

$$pK\ (\text{in } H_2O \text{ at } 25°) = 5.24 - 3.60\sigma^* \qquad (2)$$

Although pK_0 in this expression is about the same as suggested by the earlier workers, the value of ρ^* is more than doubled.

This new equation accommodates the total body of experimental information far better than the old, the

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[1] S. S. Novikov, V. M. Belikov, A. A. Fainzil'berg, L. V. Ershova, V. I. Slovetskii, and S. A. Shevelev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1855 (1959).

[2] S. S. Novikov, V. I. Slovetskii, V. M. Belikov, I. M. Zavilovich, and L. V. Epishina, *ibid.*, 520 (1962).

[3] S. S. Novikov, V. I. Slovetskii, S. A. Shevelev, and A. A. Fainzil'berg, *ibid.*, 598 (1962).

[4] V. I. Slovetskii, S. A. Shevelev, V. I. Erashko, L. I. Biryukova, A. A. Fainzil'berg, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 655 (1966).

[5] M. J. Kamlet, R. E. Oesterling, and H. G. Adolph, *J. Chem. Soc.*, 5838 (1965).

[6] H. G. Adolph and M. J. Kamlet, *J. Am. Chem. Soc.*, **88**, 4761 (1966).

[7] M. J. Kamlet and D. J. Glover, *Tetrahedron Letters*, No. 27, 17 (1960).

[8] M. J. Kamlet and D. J. Glover, *J. Org. Chem.* 27, 537 (1962).

[9] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

[10] A σ^* value of 0.99 for $CH_3C(NO_2)_2CH_2$ was obtained by applying the normal 2.8 quenching factor to $\sigma^* = 0.352$ for $CH_3C(NO_2)_2CH_2$-CH_2 as determined by J. Hine and N. C. Bailey, Jr. [*J. Org. Chem.*, **26**, 2098 (1961)], from the reaction of 4,4-dinitrovaleric acid with diphenyldiazomethane. Substituting H for CH_3 and again applying the normal quenching factor led to $\sigma^* = 1.05$ for $CH(NO_2)_2CH_2$.

[11] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).