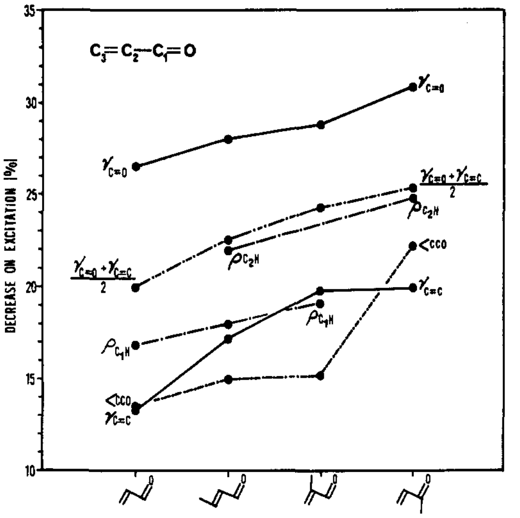

Figure 8. Percentage decrease in vibrational frequency on excitation ($S_0 \rightarrow S_1(n,\pi^*)$) for the totally symmetrical fundamentals of the singly substituted methylpropenals.

in Table VI, the best values for the two torsions are 101.1 and 111.5 cm^{-1} for the skeletal and methyl torsions, respectively.

(C) Comparison of Ground- and Excited-State Fundamentals. A tabulation of the ground-state and first-excited-singlet-state fundamentals of the singly substituted methylpropenals is presented in Table VII.

All of the molecules exhibit similar vibrational shifts upon excitation, the most significant being the drop in the carbonyl and C=C stretching frequencies, the decrease in the ∠CCO in-plane bending frequency, and the increase in the frequency of the skeletal torsion. It is interesting to note that all of the in-plane and out-of-plane hydrogen deformations exhibit a drop in frequency, which not only indicates a significant reorganization of the electron density in the mobile π system, but also an overall increase in the free valence indices at all of the carbon atoms. The percentage decrease on excitation for the totally symmetrical fundamentals of all of these compounds appears to change in a smooth manner with position of methyl group substitution. As the methyl group is attached at positions closer to the oxygen atom, the percentage decrease in frequency becomes greater (see Figure 8). This observation has important implications with respect to the mechanism through which the methyl group influences the energy and geometry of the first excited singlet state. A detailed analysis of this interaction is presented in the accompanying paper.[6]

Acknowledgments. We are grateful for the advice and criticism of Professor G. W. Robinson and wish to thank the U. S. Army Research Office (Durham) for partial financial support. We also wish to thank the Connecticut Research Commission for support of special instrumentation.

Excited-State Geometries of the Singly Substituted Methylpropenals.[1a] II. Bond Order Reversal and Substituent Interaction in $S_1(n,\pi^*)$

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Abstract: The first excited n,π^* singlet-state geometries of acrolein and its singly substituted methyl derivatives have been analyzed and compared. Excited-state bond length changes were calculated using force constant relationships and compared, where possible, to the more accurate values obtained from Franck–Condon calculations. The relative degree of bond order reversal (RDBOR) is defined and used as a quantitative measure of the degree of excited-state methyl group electron injection into Ψ_3. The methyl group was found to perturb both ground-state n-electron and excited-state Ψ_3 wave function energies *via* similar mechanisms involving "hyperconjugative" reorganization of π-system electron distribution.

Alkyl substitution normally produces a blue shift in the n → π^* transition.[2] Sidman has associated the increased energy of the transition with the electron-donating character of alkyl groups and their tendency to accumulate electronic charge in a localized region of the excited-state molecular orbital, thereby increasing its energy.[2] The present report investigates the nature of this substituent-induced blue shift for the singly substituted methylpropenals utilizing the information afforded by the vibrational analysis (discussed in the previous paper[3]) to calculated excited-state bond lengths. These bond lengths are used to define the relative degree of bond order reversal (RDBOR), a quantitative measure of the total relative electron density in the Ψ_3 (Ψ_3 is defined as the lowest antibonding π molecular orbital) molecular orbital. The latter variable assists in defining the degree of substituent (methyl group) electron injection into the singly occupied excited-state MO and allows a quantitative description

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(1) (a) Abstracted from a portion of the Ph.D. thesis of R. R. B., Wesleyan University, 1971; (b) deceased Aug 16, 1971.

(2) J. Sidman, *Chem. Rev.*, 58 689 (1958).

(3) R. R. Birge, W. C. Pringle, and P. A. Leermakers, *J. Amer. Chem. Soc.*, 93 6715 (1971).

Table I. Selected Geometric and Energetic Parameters for the $S_0(n) \rightarrow S_1(n,\pi^*)$ Transition in the Singly Substituted Methylpropenals

Assignment	$CH_2{=}CHCHO$	$CH_3CH{=}CHCHO$	$CH_2{=}C(CH_3)CHO$	$CH_2{=}CHCOCH_3$
Increase on excitation, Å				
In C=O bond[a,b]	0.117[a]	0.125[a]	0.130[b]	0.143[a]
In C=C bond[c]	0.067	0.090	0.107	0.108
RDBOR[d]	1.000	1.208	1.355	1.419
$E(S_0(n) \rightarrow S_1(n,\pi^*))$,[e] kcal	73.94	75.76	75.75	74.69
$E(S_0(n\text{ electrons}))$,[f] kcal	−232.9	−224.4	−232.4	−223.0
Rel to acrolein[f]	0.0	8.5	0.5	9.9
$E(S_1(\Psi_3))$,[g] kcal	−159.0	−148.6	−156.6	−148.3
Rel to acrolein[g]	0.0	10.4	2.4	10.7

[a] Calculated using the Franck–Condon intensity distribution analysis on carbonyl vibrational progression (see Table III). [b] Calculated by subtracting 0.006 Å from the value calculated using Badger's force constant relationship (see section I.A). [c] Calculated using Badger's relationship assuming r_e = 1.360 (Table II). [d] Relative degree of bond order reversal calculated using eq 6, 7, and 8 of section I.B (see Table IV). [e] Energies of 0, 0 bands of n → $\pi^*(\pi)$ transition (see ref 3). [f] Derived from ionization potential and solvent effect data (see Table V). [g] Calculated from the information of footnotes *e* and *f*.

of excited-state methyl group interaction. Combining this information with an analysis of substituent effects on the ground state (n electrons) indicates that the methyl group perturbs the energy of the ground and excited states primarily *via* a resonant ("hyperconjugative") π-system charge redistribution. The amount of electron injection is found to be of lesser importance than the position of the localized electron density within the molecular orbital. Sidman's original hypothesis is therefore shown to be substantially correct.

A summary of ground- and excited-state energetic and geometric parameters is given in Table I.

I. Results and Discussion

(A) Excited-State Bond Lengths. The force constant relationships of Badger[4,5] and Clark[4,6] were used to calculate excited-state carbonyl and C=C bond lengths. In addition, Franck–Condon intensity distribution calculations, which are considerably more accurate than force constant relationships, were used in the analysis of excited-state carbonyl bond lengths. A comparison of the latter calculations with the bond lengths predicted using the less reliable relationships of Badger and Clark indicates that Badger's equation is more accurate than Clark's equation for the systems investigated here. Specifically, Badger's force constant relationship differed from the Franck–Condon value (disregarding the calculation on methacrolein; see later discussion) by only 0.005–0.006 Å (about 4%). This observation is supported by a previous investigation by Craig on the excited-state bond lengths of benzene, which also indicated that Badger's relationship was more accurate than Clark's relationship when compared to the more dependable Franck–Condon calculation.[7]

Garforth, Ingold, and Poole[4] were the first investigators to use force constant relationships in calculating excited-state bond lengths. Badger's rule (eq 1) and Clark's rule (eq 2) can both be formulated in terms of the percentage of bond length increase upon excitation (eq 1a and 2a, respectively). With respect to both

$$\text{Badger's rule} \qquad k = C_{ij}(r_e - d_{ij})^{1/3} \tag{1}$$

$$\%\text{ increase} = 100(r_e - d_{ij}) \times [\{[(\omega''^2)/(\omega'^2)]^{1/3} - 1\}/r_e] \tag{1a}$$

$$\text{Clark's rule} \qquad k = C_{ij}(r_e)^{1/6} \tag{2}$$

$$\%\text{ increase} = 100[(\omega''^2/\omega'^2)^{1/6} - 1] \tag{2a}$$

relationships, k is the force constant of the bond (dynes per centimeter), r_e is the ground-state (equilibrium) bond length, C_{ij} is a universal constant (1.85×10^5) assumed to be identical in both ground and excited state, ω'' is the ground-state stretching frequency (reciprocal centimeters), and ω' is the excited-state stretching frequency. Badger's relationship includes an additional parameter, d_{ij}, which depends upon the principal quantum numbers of the bonding electrons (d_{ij} = 0.68 for carbon–carbon and carbon–oxygen bonds, 0.34 for carbon–hydrogen bonds). By assuming ground-state bond lengths (r_e) of 1.215 Å for the carbonyl group[8] and 1.360 Å for the C=C bond,[9] the excited-state bond lengths can be calculated using eq 1a and 2a (see Table II). Force constant relationships are relatively insensitive to the value chosen for the ground-state bond length. For example, an error of 0.01 Å in r_e will induce an error in calculated bond length increase of only about 0.004 Å in the carbonyl, or 0.002 Å in the C=C bond.

Franck–Condon Calculations. Franck–Condon intensity distribution calculations were used in analyzing the excited-state carbonyl stretching progressions of acrolein, crotonaldehyde, methacrolein, and methyl vinyl ketone using the closed-form overlap integral expansion developed by Craig.[7] Inuzuka[10] had previously used this expansion in the analysis of both acrolein and crotonaldehyde but limited the accuracy of his analysis to bond length changes of only ±0.01 Å. The calculations described below approach higher precision (±0.002 to ±0.004 Å) by using procedures which minimize error caused by satellite-band intensity perturbations.

The intensities of individual vibrational bands in a given vibronic progression are given by eq 3,[11] where

$$I_n = \bar{\nu}_n/\bar{\nu}_0\left[\int \Psi_0(\xi_1)\Psi_n(\xi_2)d\tau\right]^2 \tag{3}$$

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Table II. Excited-State Bond Length Changes

Bond	$CH_2{=}CHCHO$	$CH_3CH{=}CHCHO$	$CH_2{=}C(CH_3)CHO$	$CH_2{=}CHCOCH_3$
C=O stretching in				
Ground state (ω''), cm^{-1}	1723	1720	1717	1724
Excited state (ω'), cm^{-1}	1266	1238	1222	1191
Increase in C=O bond				
Badger's relationship,[a] Å	0.122	0.131	0.136	0.149
Clark's relationship,[a] Å	0.131	0.141	0.146	0.159
Franck–Condon, Å	0.117	0.125	*b*	0.143
C=C stretching in				
Ground state (ω''), cm^{-1}	1625	1644	1645	1630
Excited state (ω'), cm^{-1}	1410	1363	1320	1305
Increase in C=C bond				
Badger's relationship,[c] Å	0.067	0.090	0.107	0.108
Clark's relationship,[c] Å	0.065	0.087	0.103	0.104

[a] Calculated assuming r_e = 1.215 Å. [b] See text for discussion. [c] Calculated assuming r_e = 1.360 Å.

Table III. Franck–Condon Intensity Distribution Calculations for the C=O Progression in Acrolein, Crotonaldehyde, Methacrolein, and Methyl Vinyl Ketone

Origin separations and relative intensities							Obsd[a]	Ratios
				$CH_2{=}CHCHO$				
0.114	0.115	0.116	0.117	0.118	0.119	0.120		
1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	00
2.334	2.375	2.416	2.458	2.500	2.543	2.586	1.388	01
3.104	3.207	3.313	3.421	3.532	3.646	3.763	1.941	02
3.063	3.208	3.360	3.518	3.681	3.852	4.029	1.985	03
2.484	2.636	2.800	2.963	3.141	3.327	3.523	1.703	04
1.330	1.350	1.371	*1.392*	1.413	1.434	1.455	1.398	02/01
1.312	1.351	1.391	*1.431*	1.472	1.515	1.558	1.430	03/01
0.987	1.000	1.014	*1.028*	1.042	1.057	1.071	1.023	03/02
0.800	0.822	0.845	*0.866*	*0.889*	0.913	0.936	0.877	04/02
0.811	0.822	0.833	0.842	*0.853*	0.864	0.873	0.858	04/03
				$CH_3CH{=}CHCHO$				
0.122	0.123	0.124	0.125	0.126	0.127	0.128		
1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	00
2.654	2.698	2.742	2.786	2.831	2.876	2.921	2.025	01
3.981	4.105	4.232	4.362	4.495	4.631	4.770	3.238	02
4.407	4.604	4.808	5.020	5.240	5.468	5.705	3.725	03
3.994	4.223	4.464	4.717	4.982	5.261	5.664	3.400	04
1.500	1.521	1.543	1.566	*1.588*	*1.610*	1.633	1.599	02/01
1.661	1.706	1.753	1.802	*1.851*	1.901	1.953	1.840	03/01
1.107	1.122	1.136	*1.151*	1.166	1.181	1.196	1.150	03/02
1.003	1.029	*1.055*	1.081	1.108	1.136	1.164	1.050	04/02
0.906	*0.917*	0.928	0.940	0.951	0.962	0.974	0.913	04/03
				$CH_2{=}C(CH_3)CHO$				
0.121	0.122	0.123	0.124	0.125	0.126	0.127		
1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	00
2.600	2.643	2.686	2.730	2.774	2.819	2.864	1.426	01
3.845	3.966	4.089	4.215	4.344	4.477	4.612	2.139	02
4.216	4.405	4.601	4.805	5.016	5.235	5.462	2.491	03
3.797	4.016	4.245	4.486	4.738	5.004	5.283	2.287	04
1.479	*1.501*	1.522	1.544	1.566	1.588	1.610	1.500	02/01
1.622	1.667	1.713	*1.760*	1.808	1.857	1.907	1.747	03/01
1.097	1.111	1.125	1.143	1.155	*1.169*	1.184	1.165	03/02
0.987	1.012	1.038	*1.064*	1.091	1.118	1.145	1.069	04/02
0.901	0.912	*0.922*	0.934	0.945	0.956	0.967	0.918	04/03
				$CH_2{=}CHCOCH_3$				
0.140	0.141	0.142	0.143	0.144	0.145	0.146		
1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	00
3.474	3.524	3.574	3.625	3.675	3.727	3.779	2.716	01
6.705	6.889	7.076	7.267	7.462	7.661	7.864	5.654	02
9.436	9.808	10.193	10.590	11.000	11.424	11.862	8.012	03
1.930	1.955	1.980	2.005	2.030	2.056	*2.081*	2.082	02/01
2.716	2.783	2.851	*2.921*	*2.992*	3.065	3.138	2.950	03/01
1.407	*1.424*	1.440	1.457	1.474	1.491	1.508	1.417	03/02

[a] Observed in the vapor phase on a Cary 14 recording spectrophotometer. Value indicated is the sum of four measurements; reproducibility is better than 0.4% (±0.006), accuracy estimated at ~0.8% (±0.015).

$\bar{\nu}_0$ is the wavenumber of the band origin, $\bar{\nu}_n$ is the wavenumber of the *n*th band in the progression, and $\Psi_i(\xi_j)$ represents the *i*th simple harmonic oscillator wave function of the *j*th electronic state ($j = 1 =$ ground state). The overlap integral can be expanded in closed form as a function of ρ ($=\omega''/\omega'$), the ratio of ground- to excited-state stretching frequencies, and q, the separation or origins between ground- and excited-state oscillator wave functions (*i.e.*, increase in C=O bond length) in ångströms[7] (eq 4). With respect to

$$\int \Psi_0(\xi_1)\Psi_n(\xi_2)\mathrm{d}\tau = (e^{-\beta_1\{q^2/2(1+\rho)\}}) \sum_r \left\{\frac{\sqrt{\beta_2}(q\rho)}{1+\rho}\right\}^{n-r} \left\{\frac{n!}{r!(n-r)!}\right\}^{1/2} \times \left\{\frac{2^{n-r}}{(n-r)!}\right\}^{1/2} S_{0r} \quad (4)$$

eq 4, $\beta_j = (2\pi/h)\sqrt{mk_j}$, where m is the reduced mass of the carbonyl group (1.1392×10^{-23} g), k_j is the bond force constant in state j, and r is a summation integer equal to, or less than, the progression (vibrational quantum) number n. S_{0r} represents the elementary overlap integral between oscillator wave functions about a common origin and is given by eq 5.[7] S_{0r} vanishes for odd values of r, as would be predicted by elementary overlap considerations for odd-numbered (*e.g.*, 0 → 1, 0 → 3) transitions.

$$S_{0r} = \frac{1}{(r/2)!}\sqrt{\frac{r!}{2^r}}\left(\frac{2\sqrt{\rho}}{1+\rho}\right)^{1/2}\left(\frac{1-\rho}{1+\rho}\right)^{r/2} \quad (5)$$

The above calculating procedure introduces two possible errors which should be considered. Since the carbonyl group is treated as a simple diatomic molecule which is harmonically bound, vibrational mixing of the carbonyl stretching with other vibrations in the molecule, introducing anharmonicity in the vibrational progression and oscillator strength variations due to intensity borrowing, will adversely affect calculated parameters. Although it is difficult to predict in which direction the mixing will perturb the calculated value of the origin separation (q), the presence of vibrational mixing can usually be uncovered in the analysis of the vibronic spectrum. We would not expect vibrational mixing to exhibit equivalent interaction in different quantum vibrational states. Therefore, a spread in calculated origin separations at different transition ratios provides a secondary check on the importance of vibrational mixing. As can be seen in Table III, this source of error appears largest in methacrolein and methyl vinyl ketone, moderate in crotonaldehyde, and small in acrolein. This observation is consistent with an expected perturbation, induced by a C–CH_3 totally symmetrical in-plane valence stretching, becoming increasingly significant in those molecules in which the methyl group is in close proximity to the carbonyl oscillator.

A more significant error, however, is introduced by assuming that the intensity of the band is directly proportional to the observed optical density and ignoring the contribution of closely spaced, partially overlapping satellite bands. This source of intensity perturbation is important in the molecules investigated here because of the complicated and closely spaced band structure associated with the vibronic spectra. Two experimental and analytical procedures were used to minimize this type of error: (1) optical densities were recorded with a spectral band width resolution (0.3–0.4 Å) close to the natural bandwidths of the vibronic bands, (2) calculated relative intensities were compared to experimental relative intensities only for band pairs which had very similar satellite band environments. The second limitation required that the system origin no longer be the basis for relative comparison, since this band has a totally different satellite environment than the remaining progression members. Consequently, the analysis (presented in Table III) compares (where possible) the calculated intensity ratios between band pairs 02/01, 03/01, 03/02, 04/02, and 04/03 with the ratios observed experimentally. The small spread in calculated origin separations for various band intensity ratios in the case of the acrolein calculation lends credence to this approach.

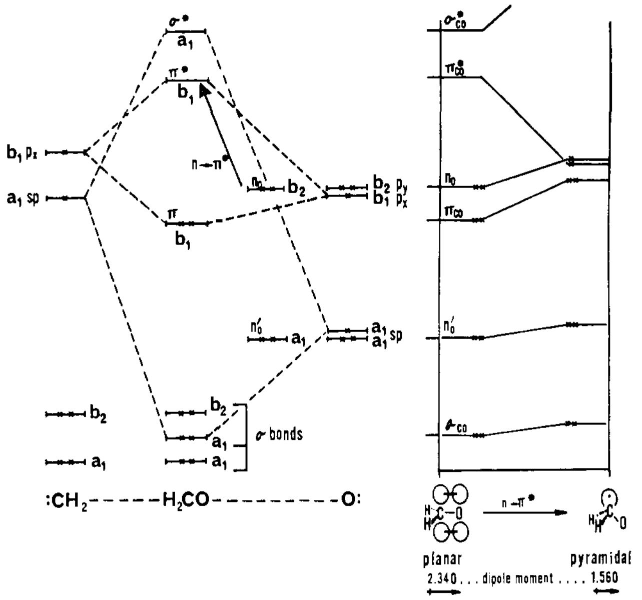

Figure 1. The n → π^*(p) transition in formaldehyde. The correlation diagram is adapted from A. D. Walsh, *J. Chem. Soc.*, 2306 (1953); the dipole moments are from D. E. Freeman, J. R. Lombardi, and W. Klemperer, *J. Chem. Phys.*, **45**, 58 (1966).

Acrolein (q = 0.117 ± 0.001 Å), crotonaldehyde (q = 0.125 ± 0.002 Å), and methyl vinyl ketone (q = 0.143 ± 0.003 Å) are molecules for which the carbonyl stretching frequency forms the only prominent band progression in the electronic spectrum. Methacrolein, however, exhibits a second strong progression in the C=C stretching vibration which complicates the carbonyl absorption bands with its own satellite system. For the above reason, as well as the vibrational mixing intensity perturbations discussed in the previous paragraph, the calculations for methacrolein cannot be relied upon to give accurate results. The somewhat haphazard deviations among the q values calculated for different band intensity ratios is a manifestation of these experimental problems.

(B) Excited-State Bond Order Reversal. Two mechanisms, hybridization or resonant delocalization, may operate in the stabilization of carbonyl n,π^* singlet and triplet states. The former mechanism is associated with aliphatic carbonyl compounds and involves the partial hybridization of the carbonyl carbon from a planar sp^2 toward a nonplanar sp^3 electronic structure to lower the energy of the π^* antibonding orbital and concentrate the excited-state electron in an orbital associated primarily with the carbon atom. The most thoroughly studied example is formaldehyde, which is shown in Figure 1. This type of transition will be designated as n → π^*(p) to

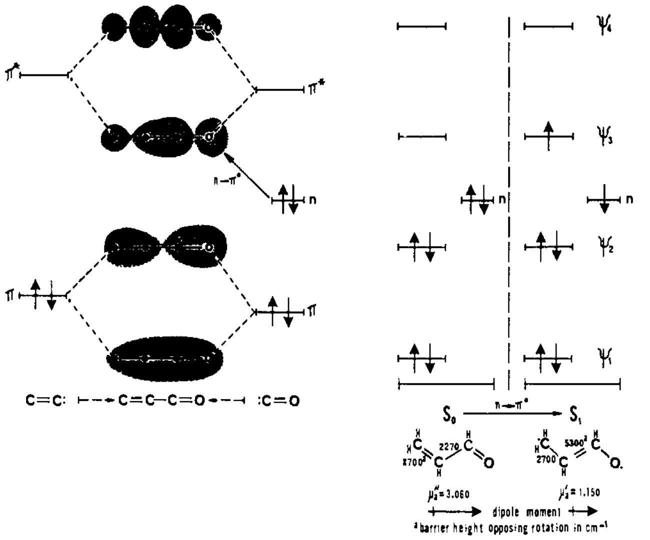

Figure 2. n → $\pi^*(\pi)$ transition in acrolein. The barrier heights are from ref 18; the dipole moments are from D. A. Haner and D. A. Dows, *J. Mol. Spectrosc.*, **34**, 296 (1970).

indicate that the nonbonding electron is promoted into a semilocalized p (sp^3) type orbital. Although a pyrimidal n,π^*(p) geometry has only been spectroscopically verified for small molecules like formaldehyde,[12] formyl fluoride,[13] carbonyl chloride,[14] and cyclopentanone,[15] recent absorption[16] and emission[17] work has indicated that nonplanar n,π^*(p) excited states of aliphatic carbonyl systems are probably the rule rather than the exception.

A second type of n,π^* excited-state stabilizing mechanism is associated with molecules, like those investigated in this paper, in which the carbonyl group is in resonance with an α unsaturated group. This mechanism, which stabilizes the excited state *via* resonant delocalization of the electron within the mobile π system, is generally more effective than hybridization in lowering the energy of an n,π^* state (For example, the 0, 0 band for the n → π^*(p) transition in formaldehyde is 80.76 kcal[12] while the 0, 0 band for the n → π^* transition in acrolein is 73.94 kcal,[18] a net stabilization of 6.82 kcal.) This second type of transition will be designated as n → $\pi^*(\pi)$ to indicate that the nonbonding electron is promoted into a delocalized π molecular orbital, as shown in Figure 2 for acrolein. Clearly, each stabilization mechanism is mutually exclusive with respect to the other, since resonant stabilization requires planarity which hybridization destroys. Because of the different excited-state geometries of n,π^*(p) *vs.* n,$\pi^*(\pi)$ states, the mechanisms of excited-state substituent interaction can prove to be vastly different between the two classes. Consequently, *the present discussion on the n → $\pi^*(\pi)$ transition in the propenals should be considered applicable only for n → $\pi^*(\pi)$ type transitions.*

Resonant delocalization in n,$\pi^*(\pi)$ states can be spectroscopically verified by observation of π-system bond order reversal. In the case of the substituted propenals, the bond order reversal results from the promotion of an electron into the antibonding Ψ_3 molecular orbital (Figure 2). The degree of bond order reversal is a measure of the electron density in Ψ_3 and is a useful variable in determining the mechanism through which a given substituent perturbs the energy of the excited state of the molecule.

For the purpose of quantitative comparisons, the relative degree of bond order reversal (RDBOR) will be defined as follows.

$$\text{rdbor(C=O)} = \frac{\text{\% increase in C=O bond length in compound}}{\text{\% increase in C=O bond length in standard}} \qquad (6)$$

$$\text{rdbor(C=C)} = \frac{\text{\% increase in C=C bond length in compound}}{\text{\% increase in C=C bond length in standard}} \qquad (7)$$

$$\text{RDBOR} = (1/2)[\text{rdbor(C=O)} + \text{rdbor(C=C)}] \qquad (8)$$

Equations 6 and 7 define the localized bond order reversals associated with the carbonyl and C=C groups relative to acrolein (standard), while eq 8 combines the localized functions to define the bond order reversal for the molecule as a whole. The percentage change in bond length (upon excitation) is calculated using Badger's force constant relationship (eq 1a). The results of these calculations for the singly substituted methylpropenals are shown in Table IV. The large variation in bond order reversal as a function of the position of the methyl group is mechanistically interesting and indicates that the methyl group is interacting to varying degrees with the singly occupied antibonding Ψ_3 molecular orbital increasing its electron density. The mechanism of methyl group interaction will be discussed in greater detail in the following section.

Table IV. Relative Degree of Bond Order Reversal in the First Excited Singlet States of the Substituted Methylpropenals

Compound	rdbor-(C=O)	rdbor-(C=C)	RDBOR
Acrolein	1.000	1.000	1.000
Crotonaldehyde	1.075	1.341	1.208
Methacrolein	1.116	1.593	1.355
Methyl vinyl ketone	1.225	1.612	1.419

II. Mechanisms of Methyl Group Interaction

(A) Ground-State Substituent Interaction. Before discussing substituent-induced perturbations in the energy of the Ψ_3 molecular orbital, the effect of methyl group position on the energy of the ground-state nonbonding electrons on oxygen will be discussed. The energy of these lone-pair electrons is directly related to the ionization potential of the molecule.[19-22] Ioniza-

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[20] J. D. Morrison and A. J. C. Nicholson, *ibid.*, **20**, 1021 (1952).

[21] A. D. Walsh, *Trans. Faraday Soc.*, **43**, 158 (1947), and earlier papers.

[22] D. Cook, *J. Amer. Chem. Soc.*, 80, 49 (1958).

Table V. Ionization Potential and Solvent Effect Data for the Singly Substituted Methylpropenals

Assignment	$CH_2{=}CHCHO$	$CH_3CH{=}CHCHO$	$CH_2{=}C(CH_3)CHO$	$CH_2{=}CHCOCH_3$
Ionization potential, eV				
Photoionization[a]	10.10	9.73		
Electron impact[b]	10.34			9.91
Rel to acrolein	0.00	0.37		0.43
$\bar{\nu}$ (max, n → π^*), cm^{-1}				
Ethanol	30,200	31,455	30,760	31,220
Hexane	29,800	30,500	30,335	30,230
$\Delta\bar{\nu}$ (rel to acrolein)	000	555	25	590
E(n) (rel to acrolein), kcal	0.0[a,b]	8.5[a]	~0.5[c]	9.9[b]

[a] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). [b] J. D. Morrison and A. J. C. Nicholson, *ibid.*, **20**, 1021 (1952). [c] Calculated from solvent effect data (see text).

tion potential data were available for acrolein,[19,20] crotonaldehyde,[19] and methyl vinyl ketone[21] vapors. The energy of the n electrons in methacrolein (relative to acrolein) was calculated from solvent polarity shifts.[23] The compiled data are presented in Table V.

Walsh was one of the first investigators to recognize the importance of electron density (or polarity) on the energy of the lone-pair electrons on oxygen.[21] As electron density is increased at the oxygen atom, the sizes of all of the atomic orbitals increase due to electronic repulsion and nuclear shielding, causing a net increase in the energies of all of the oxygen atomic wave functions. Consequently, the ionization potential correlates well with other experimental variables which are directly or indirectly affected by carbonyl polarity. Figure 3 shows the correlation of the energy of the n electrons (relative to acrolein) with dipole moment, solvent effects on carbonyl stretching, and electronic absorption frequencies, and charge on oxygen as calculated using simple molecular orbital theory.[24] In summary, therefore, *electron-donating substituents, added at positions which tend to increase the electron density at oxygen, will simultaneously increase the energy of the n electrons on oxygen.*

The methyl group is an inductomesomeric electron donor which perturbs the ground-state charge distribution of unsaturated molecules in an "alternating" fashion.[25] Reliable calculations using both CNDO/2[25a] and LCAO-SCF[25b] theories indicate that most of the electron reorganization occurs through resonant "hyperconjugative" π-system redistribution rather than inductive effects involving the σ system. Our observations support this conclusion. The high ground-state energies (n electron) of crotonaldehyde and methyl vinyl ketone relative to acrolein appear to result primarily from methyl-group-induced resonant reorganization of the π-system charge distribution resulting in increased electron density at oxygen. A simple molecular orbital calculation using an inductive-conjugative model of the methyl group provides fairly reliable quantitative comparisons and is shown in Figure 4.[24] The methyl group in methacrolein is substituted β to the oxygen atom and, on the basis of both charge alternation resonance structures and simple MO theory (Figure 4), would be expected to have little effect on the electron density of oxygen. This prediction is experimentally verified. The infrared analysis indicates, however, that the $\sigma(CH_3)-(\Psi_1 +$

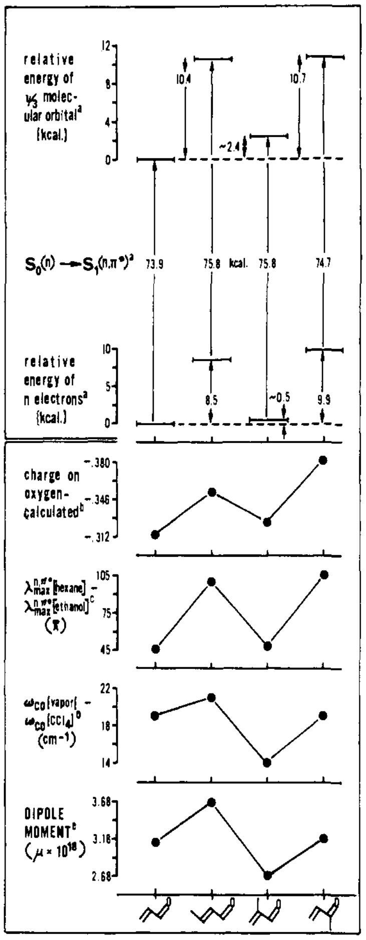

Figure 3. Relative energies of ground and excited states and correlation of "n" electron energies with various experimental and calculated parameters measuring carbonyl group polarity: (a) see Table I; (b) calculated using HMO-LCAO-SCF (ω) techniques (see section III); (c) see Table V; (d) vapor- and liquid-phase carbonyl stretching frequencies taken from Table V of accompanying paper;[3] (e) R. D. Nelson, D. R. Lide, and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase," NSRDS-NBS 10, U. S. Government Printing Office, Washington, D. C.

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(23) For similar carbonyl systems and identical electronic transitions [*e.g.*, n → $\pi^*(\pi)$], the degree of energy shift in the absorption maximum on changing solvent polarity is a function of the charge on oxygen in the ground and (to a lesser extent) excited states. Consequently, an almost linear relationship is found between ionization potential and solvent polarity shifts, and graphical extrapolation can be used to calculate lone-pair electron energies. Such an analysis on the methylpropenals places the ground-state energy of methacrolein at 0.43 ± 0.03 kcal/mol (above acrolein) assuming no error in $\bar{\nu}_{max}$ data. Including this source of error, the relative energy is 0.43 ± 0.37 or simply ~0.5 kcal/mol.

(24) See Appendix for details of the calculation.

(25) (a) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967); W. J. Hehre and J. A. Pople, *ibid.*, **92**, 2191 (1970); (b) M. D. Newton and W. N. Lipscomb, *ibid.*, **89**, 4261 (1967).

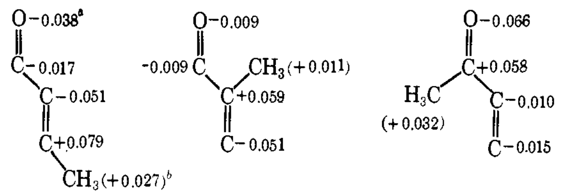

Figure 4. Methyl-induced charge distributions (relative to acrolein) in the singly substituted methylpropenals (calculated using HMO–LCAO–SCF (ω) techniques; see Appendix): (a) these are relative π-system charge distributions and should not be confused with absolute charge distributions; (b) values in parentheses are the total charges on the methyl group; *i.e.*, a total charge of +0.024 on CH_3 means that the methyl group has injected −0.024 charge unit into the π system of the particular compound.

Ψ_2) interaction in crotonaldehyde does not involve the appreciable bond order perturbations predicted by classical hyperconjugative resonant structures like the following.

(B) Excited-State Substituent Interaction. A knowledge of relative ground-state (n electron) and 0, 0 band (n,π*) energies permits the calculation of relative Ψ_3 (of the n,π* system) energies necessary in analyzing excited-state methyl group interaction. It is instructive to compare the degree of bond order reversal, which is a measure of the degree of methyl group electron injection into Ψ_3, with the excited-state energies (see Table VI). As can be seen in Table VI, the degree of methyl group electron injection (RDBOR) does not correlate with $E(\Psi_3)$. Apparently, the charge reorganization induced through "hyperconjugative" interaction of the methyl group with the π system is a more influential variable. In other words, the mode of destabilization is similar for both the ground and excited states. This similarity can be explained if one assumes that the electron density in Ψ_3 is polarized toward the electron-deficient (n,π*) oxygen atom.[26] Under these circumstances, *the inductomesomeric electron-donating methyl group would destabilize Ψ_3 when substituted at positions which direct negative charge into the carbonyl system and increase the polarized imbalance of the Ψ_3 molecular orbital.* Consequently, the methyl groups in crotonaldehyde and methyl vinyl ketone would destabilize Ψ_3 for reasons similar to those used in explaining ground-state destabilization mechanisms. Methacrolein would be expected to exhibit a minimal destabilization.

Table VI. Relative Ground- and Excited-State Energies for the n → π*(π) Transition in the Singly Substituted Methylpropenals

Compound	$E(n)^a$	$E(\Psi_3)^a$	$E(\Psi_3) - E(n)^a$	RDBOR^b
Acrolein	0.0	0.0	0.0	1.000
Crotonaldehyde	8.5	10.4	1.9	1.203
Methacrolein	0.5	2.4	1.9	1.355
Methyl vinyl ketone	9.9	10.7	0.8	1.419

[a] Relative to acrolein; kilocalories per mole. [b] Relative degree of bond order reversal (see Table IV).

Although substituent-induced Ψ_3 electron reorganization accounts for a major portion of the destabilization in crotonaldehyde and methyl vinyl ketone, the observation that the methyl group injects electron density into the total Ψ_3 wave function must also be considered as a source of destabilization. While it probably accounts for less than 20% of the net perturbation in the former two compounds, the 2.4-kcal destabilization in the excited state of methacrolein is probably predominantly a function of the overall electron–electron repulsion induced in the total Ψ_3 wave function caused by substituent electron injection. The latter observation is supported by singlet–triplet splitting data.[28]

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Appendix. Molecular Orbital Calculations

Streitwieser's success in calculating ionization potentials for methyl-substituted unsaturated systems using the ω technique (HMO–LCAO–SCF(ω))[29,30] prompted us to investigate this procedure for calculating ground- and excited-state parameters for the methylpropenals. A preliminary investigation of four models for the methyl group, the heteroatom,[30,31] the inductive,[32] the conjugative,[29] and the inductive-conjugative,[29] indicated that bond orders and charge distributions were best described using the latter model. The inductive-conjugative model treats the methyl group as a modified vinyl group, and, consequently, the methyl group is introduced into the secular determinant as a two-atom component with Coulomb and bond-integral parameters appropriately modified. This approach was originally proposed by Mulliken and coworkers.[33]

The ground-state parameters chosen for the methyl group[29] ($h_C = -0.3$, $h_X = -0.3$, $h_Y = -0.6$, $k_{C-X} = 0.8$, $k_{X=Y} = 2.8$ ($-C\equiv H_3 \equiv -CX\equiv Y$)), oxygen[30] ($h_O = 1.1$, $k_{C=O} = 0.8$), and carbon[30] ($h_C = 0.0$ (-0.3 when $-CH_3$ group is attached), $k_{C-C} = 1.05$, $k_{C=C} = 0.9$) are those of Streitwieser,[29,30] with the exception of the oxygen Coulomb integral, which is our own.[34] The value for the Coulomb integral of oxygen in the excited state was calculated by subtracting 1.0 from the ground-state value to compensate for the local electron density decrease caused by the excitation of one of the lone-pair electrons of oxygen into the delocalized antibonding MO (*i.e.*, h_O^{n,π^*} =

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[26] The observation that the carbonyl group in acrolein experiences a much larger n → π* excitation-induced bond order reversal than the vinyl group indicates that Ψ_3 concentrates a significant proportion of its electron density at the carbonyl system. This finding is further supported by the first excited n,π*(π) singlet dipole moments of acrolein[27a] and propynal[27b] which are only ~1.4 D less than the ground-state values.

[27] (a) D. A. Haner and D. A. Dows, *J. Mol. Spectrosc.*, **34**, 296 (1970); (b) D. E. Freeman, J. R. Lombardi, and W. Klemperer, *J. Chem. Phys.*, **45**, 58 (1966).

[28] R. R. Birge and P. A. Leermakers, results to be published in part III of this series.

[29] A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).

[30] A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **82**, 4123 (1960).

[31] F. A. Matsen, *ibid.*, **72**, 5243 (1950).

[32] E. L. Mackor, A. Hofstra and J. H. Van der Waals, *Trans. Faraday Soc.*, **54**, 186 (1958).

[33] R. S. Mulliken, C. A. Rieckc, and W. G. Brown, *J. Amer. Chem. Soc.*, 63, 41 (1941).

[34] The Coulomb integral for the carbonyl oxygen ($h_O = 1.1$) used in these calculations is considerably smaller than the value proposed by Streitwieser ($h_O = 1.3$; ref 30). Nevertheless, it appears that this parameter must be reduced even more if calculated electron densities at oxygen are to compare more favorably with more advanced MO theory.[25]

Table VII. Comparison of Calculated (HMO–LCAO–SCF(ω)) and Experimental Parameters[a]

No.	Assignment	$CH_2{=}CHCHO$	$CH_3CH{=}CHCHO$	$CH_2{=}C(CH_3)CHO$	$CH_2{=}CHCOCH_3$
1	Charge on $O(S_0)$	−0.314	−0.352	−0.323	−0.380
2	Rel E(n),[a] kcal	0.0	8.5	0.5	9.9
	Decrease in bond order on excitation				
3	C=O	0.2232	0.2099	0.2332	0.1880
4	C=C	0.1513	0.1085	0.1281	0.1827
5	C=O + C=C	0.3745	0.3184	0.3613	0.3707
6	RDBOR[b]	1.000	1.208	1.355	1.419
	Bond order for C_1—C_2				
7	In ground state	0.4602	0.4958	0.4538	0.4319
8	In excited state (n,π^*)	0.5584	0.5487	0.5504	0.5559
9	Increase on excitation	0.0982	0.0529	0.0966	0.1240
	Skeletal torsions,[c] cm^{-1}				
10	In ground state	158	206	163	101
11	In excited state (n,π^*)	250	243	233	230
12	Increase on excitation	92	37	70	129
	Methyl group electron injection				
13	In ground state		−0.027	−0.011	−0.032
14	In excited state (n,π^*)		−0.315	−0.328	−0.321
15	Excited/ground		11.7	29.8	10.0
16	Rel $E(\Psi_3)$/rel E(n)[d]		1.22	4.80	1.08

[a] Energy of n electrons relative to acrolein; see Table V. [b] Relative degree of bond order reversal; see Table IV. [c] See Table VI of ref 3. [d] Energy of Ψ_3 molecular orbital divided by energy of n electrons with both energies relative to acrolein (see Table VI).

0.1). All remaining parameters were not altered in excited-state calculations so that variations in bond order and electron density on excitation could be compared without concern that a major portion of these observed perturbations were a function of parameter changes rather than the interaction of the singly occupied excited state MO.

All of the ground-state calculations reached self-consistence in fewer than ten iterations. Excited-state calculations, however, required close to 20 iterations, probably because of the charge perturbations introduced by an additional interacting molecular orbital. The iterative constant, ω, was given the well-established value of 1.4 (ref 30).

The results of some of the calculated parameters[35] are compared with observed data in Table VII. In general, the calculations are very good for ground-state parameters. For example, the electron density at oxygen compares favorably with the relative energy of the lone-pair electrons (rows 1 and 2). Excited-state predictions, however, were variable in quality. For example, while the ω technique correctly predicts that the carbonyl group will experience a greater localized bond order reversal than will the vinyl C=C group (rows 3 and 4), it erroneously predicts that acrolein will have the greatest total bond order reversal (row 5). This error is traceable to the inductive-conjugative model used for the methyl group, which, by incorporating resonant interaction in the simple MO theory, increases the total π-system matrix, thereby decreasing localized bond order effects. Within the singly substituted derivatives, however, the total bond order reversal (RDBOR) is qualitatively predicted (rows 5 and 6). A more encouraging success for this model, however, is found in comparing central C–C bond order increase on excitation with the experimentally observed increase in skeletal torsion. The correlation (compare rows 9 and 12) is surprisingly good and indicates that our model for the methyl group is qualitatively useful. In further support of this conclusion, these simple calculations also qualitatively predict the relative amount of ground- *vs.* excited-state methyl group electron injection (rows 13 and 14). The ratio of excited- to ground-state electron injection should vary as the ratio of the relative excited- (Ψ_3) and ground- (n electron) state energies.[36] Consequently, rows 15 and 16 should exhibit qualitative agreement and the almost linear relationship observed is most encouraging.

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[35] All calculated bond orders and charge distributions listed in Table VII are derived from eigenvectors which are accurate, with respect to self-consistence, to better than four significant figures. The normal procedure of limiting analysis to a single iteration,[29,30] while adequate for ground-state parameters, would produce significant error for the excited-state calculations.

[36] The methyl group perturbs both ground and excited states *via* similar mechanisms involving the resonant reorganization of π-system electron density. The amount of π-density reorganization is directly proportional to the amount of substituent electron injection. Consequently, for a given molecule, the ratio of substituent electron injection in ground and excited states should vary as the ratio of induced energy perturbations in both states (rows 15 and 16).