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# Conformational Analysis. CXII. Conformations, Energies, and Electronic Absorption Spectra of $\alpha,\beta$-Unsaturated Aldehydes and Ketones[1,2]

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**Abstract:** A previously described molecular mechanics method for the calculation of the structures and energies of hydrocarbons with delocalized electronic systems has been extended to include molecules containing a conjugated carbonyl group. In cases where a comparison with experimental data can be made, the agreement is good. Electronic spectra were calculated using a VESCF method including doubly excited states in the configuration interaction. The presence of two $\pi \rightarrow \pi^*$ transitions close to the observed absorption maxima, not found in calculations employing only singly excited states, is indicated by these calculations.

In previous papers a molecular mechanics method for the calculation of structures and energies of hydrocarbons with delocalized electronic systems was developed.[4,5] This method includes a quantum mechanical $\pi$ system calculation (VESCF) in the iterative energy minimization sequence. The purpose of the VESCF calculation is to provide bond orders, from which the stretching and torsional force constants for the conjugated system are deduced. Calculations on a variety of conjugated hydrocarbons generally yielded structures and energies in good agreement with experimental data.

## The Method

In the present paper is described an extension of the force field for delocalized hydrocarbon systems to include compounds containing a carbonyl group. Conformations and energies of $\alpha,\beta$-unsaturated aldehydes and ketones will be discussed. Since there is a continued interest in the spectroscopic properties of these molecules,[6-8] we have also calculated their electronic spectra by the VESCF-Cl method,[5,9-11a] including all singly and doubly excited electronic configurations, and using geometries obtained from the force field calculations. The resonance and two-center repulsion integrals were calculated as described in ref 5.[11b]

**Parameters.** The basic force field used in the present work is essentially the same as previously described.[4,5] A number of new parameters, specific for the conjugated carbonyl system, were evaluated by fitting calculated values to experimental data. The data used in the parameterization were the electron diffraction structure of acrolein;[12,13] the cis-trans energy difference for acrolein,[14] 3-buten-2-one[15] (methyl vinyl ketone), and methacrolein;[16] and the barrier to internal rotation in acrolein.[14] The value for the cis-trans energy difference in methacrolein had to be taken from liquid-phase experiments, as a vapor-phase value is not available. A comparison of the cis-trans energy differences in 3-buten-2-one and *trans*-pent-3-en-2-one in solution and in the vapor phase suggests that the inconsistency is small.[15] The parameters involving the unsaturated carbonyl system are summarized in Table I.

Attempts to reproduce the barriers to methyl group rotation in 3-buten-2-one, methacrolein, and crotonaldehyde met with some difficulties. In previous work[17] it was found that no torsional contribution for eclipsing a methyl group hydrogen and a double bond was necessary to reproduce the barrier to methyl group rotation in propene and other simple (unconjugated) alkenes. However, using the same approach and numerical values for methacrolein, essentially free rotation of the methyl group was calculated. The experimental barrier is 1.34 ± 0.06 kcal/mol (microwave).[18] Similarly, the corresponding barrier in isoprene was calculated to be only about half of that experimentally observed.[19a] Logically, it would seem that the torsional constant for a methyl attached to an unsaturated carbon should not in general be a constant, but should be a function of the bond order. The torsional force constants for eclipsing pure single and double bonds, respectively, were therefore used to construct a linear relationship between bond order and torsional constant. The latter were then calculated from the former using this relationship for different molecules as needed.[19b] No new parameters were necessary. This approach gave barriers to methyl group rotation in isoprene, methacrolein, and crotonaldehyde of 2.88, 1.53, and 1.82 kcal/mol, respectively. The calculated values compare favorably with the experimental ones 2.62,[19a] 1.34,[18] and 1.73[20] kcal/mol, respectively. Satisfactory barriers were calculated for *cis*- and *trans*-1,3-pentadiene, 0.55 and 1.83 kcal/mol, respectively (experimental[21] 0.74 and 1.81 kcal/mol). Similar calculations on hydrocarbons were reported earlier by Dodziuk.[22] Since the bond orders at the $\alpha,\beta$ bond for the compounds considered in this paper are quite similar, a single value for the torsional contribution, $V_3 = 1.37$ kcal/mol (see Table I), was used, which corresponds to the bond order calculated for the central bond in acrolein. In the general case the calculation of the torsional parameter should be made part of the computer program. The same

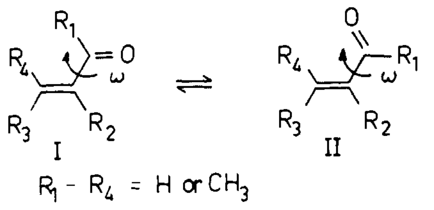

**Figure 1.** Definition of substituents.

**Table I.** Force Field Parameters[a]

van der Waals Constants

| Atom | $r^*$, Å | $\epsilon$, kcal/mol |
|---|---|---|
| O | 1.65 | 0.046 |

Natural Bond Lengths and Stretching Force Constants

| Bond | $l_0$, Å | Slope $(l_0)$[b] | $k_l$, mdyn/Å | Slope $(k_l)$[b] |
|---|---|---|---|---|
| $\mathrm{C_{sp^2}{-}C_{CO}}$[c] | 1.351 | 0.179 | 9.60 | 4.60 |
| $\mathrm{C{=}O}$ | 1.207 | 0.105 | 10.80 | 4.60 |

Cubic stretching constant = −2.0

Natural Bond Angles and Bending Force Constants

| Angle | $\theta_0$, deg | $k_\theta$, mdyn Å/rad$^2$ |
|---|---|---|
| $\mathrm{H{-}C{=}O}$ | 120.6 | 0.25 |
| $\mathrm{H{-}C_{CO}{-}C_{sp^2}}$ | 112.0 | 0.40 |
| $\mathrm{C_{sp^2}{-}C{=}O}$ | 124.5 | 0.50 |
| $\mathrm{C_{sp^2}{-}C_{sp^2}{-}C_{CO}}$ | 117.6 | 0.60 |
| $\mathrm{H{-}C_{sp^2}{-}C_{CO}}$ | 120.0 | 0.24 |
| $\mathrm{C_{sp^3}{-}C_{sp^2}{-}C_{CO}}$ | 120.0 | 0.38 |
| $\mathrm{C_{sp^3}{-}C_{CO}{-}C_{sp^2}}$ | 115.0 | 0.40 |
| $\mathrm{C_{sp^2}{-}C_{CO}{-}C_{sp^2}}$ | 115.0 | 0.60 |

Cubic bending constant = −0.006

Torsional Constants

| Angle | $V_1$ | $V_2$, kcal/mol | $V_3$ |
|---|---|---|---|
| $\mathrm{C_{sp^3}{-}C_{sp^2}{=}C_{sp^2}{-}C_{CO}}$ | | 16.25[d] | |
| $\mathrm{H{-}C_{CO}{-}C_{sp^2}{-}C_{sp^3}}$ | 1.13 | 10.38 | |
| $\mathrm{C_{sp^2}{=}C_{sp^2}{-}C{=}O}$ | 0.91[e] | 10.38 | 0.91[e] |
| $\mathrm{C_{sp^3}{-}C_{sp^2}{-}C{=}O}$ | | 10.38 | |
| $\mathrm{H{-}C_{sp^2}{-}C{=}O}$ | | 10.38 | |
| $\mathrm{C_{sp^2}{=}C_{sp^2}{-}C_{CO}{-}H}$ | | 10.38 | |
| $\mathrm{C_{sp^2}{=}C_{sp^2}{-}C_{CO}{-}C_{sp^3}}$ | 0.15 | 10.38 | |
| $\mathrm{H{-}C_{sp^2}{-}C_{CO}{-}H}$ | | 10.38 | |
| $\mathrm{H{-}C_{sp^2}{-}C_{CO}{-}C_{sp^3}}$ | | 10.38 | |
| $\mathrm{C_{sp^3}{-}C_{sp^2}{-}C_{CO}{-}C_{sp^3}}$ | | 10.38 | |
| $\mathrm{C_{sp^3}{-}C_{sp^2}{-}C_{CO}{-}C_{sp^3}}$ | | 10.38 | |
| $\mathrm{H{-}C_{sp^3}{-}C{=}O}$ | | | −0.73 |
| $\mathrm{C_{sp^2}{-}C_{CO}{-}C_{sp^3}{-}H}$ | | | −0.75 |
| $\mathrm{H{-}C_{sp^3}{-}C_{sp^2}{-}C_{CO}}$ | | | 1.37 |

[a] For notations see ref 4, 5, and 17. [b] These are slopes defining linear bond order–bond length and bond order–force constant relations.[4] [c] $\mathrm{C_{CO}}$ = carbonyl carbon. [d] All $V_2$ torsional constants for rotation around a $\mathrm{C_{sp^2}{=}C_{sp^2}}$ bond are given this value. For other parameters involving such bonds see ref 17. [e] These terms were obtained from a comparison between the experimental and calculated potential curves for internal rotation in acrolein.[14]

idea was employed to calculate the barrier to methyl group rotation in 3-buten-2-one. In this case the calculated barrier, 2.21 kcal/mol, is significantly higher than the experimental one, 1.25 kcal/mol.[23] Several modifications of the force field parameters did not improve the situation. We feel that the experimental barrier is surprisingly low, almost the same as in acetaldehyde (1.15 kcal/mol[24]). In comparison, the barrier to methyl group rotation in isoprene is 0.6 kcal/mol higher than the corresponding barrier in propene,[19a,25] which the calculations reproduce and indicate to be a result of a steric interaction with the terminal methylene group. The discrepancy was not resolved.

The parameter set was tested by calculating the barriers to rotation in benzaldehyde and acetophenone for which accurate vapor phase data are available. The calculated barriers, 4.90 and 3.14 kcal/mol, respectively, are in good agreement with the experimentally observed values, 4.90[26] and 3.1[27] kcal/mol, respectively. This slightly extended force field was then used to calculate conformations and energies of $\alpha,\beta$-unsaturated aldehydes and ketones, shown in Figure 1.

## Conformations and Energies

A wealth of spectroscopic data on $\alpha,\beta$-unsaturated carbonyl compounds has been accumulated, and in many papers these data have been used to estimate the preferred conformations of these compounds.[6,7,28,29] The intensities of ir and uv absorptions have been especially useful for distinguishing between s-cis and s-trans conformers. There have, however, been very few attempts to calculate the conformational properties of this class of compounds. The great flexibility of enones suggests that only a calculational approach in which the energy of the molecule is minimized with respect to all coordinates is likely to yield useful results. Such an approach is not yet practical if ab initio methods are to be used, due to the prohibitive amounts of computer time involved in such calculations for molecules of the size considered in this paper. In a recent paper,[30] Dodziuk used a molecular mechanical model to calculate structures and energies of a few acrolein derivatives.

The results of our calculations and the available experimental data are given in Table II. In all cases two local energy minima were found, which may be called s-cis and s-trans forms. These are planar in many simple cases, but more generally there is a form with a torsional angle $0° \le \omega \le 90°$ ($\omega_1$) and another for $90° \le \omega \le 180°$ ($\omega_2$), where $\omega = 0$ and 180° correspond to the s-cis and s-trans forms, respectively. The $\Delta E(90° - \omega_2)$ values in Table II represent the barrier to interconversion from I to II (Figure 1). In the highly substituted molecules **2d** and **2f–h**, it was found that the torsional angle for the energy maximum between the two stable conformations deviated significantly from 90°. The calculated barriers for these cases will be discussed below (see also Figure 2).

Only a few quantitative experimental data are available for a comparison with calculated values. Furthermore, most of the former were obtained from liquid-phase experiments. In those cases where comparisons can be made the agreement is satisfactory (Table II), except that the calculated barrier for methacrolein (**1b**) is significantly lower than the observed one. This latter value is, however, suspiciously high when compared with the observed barrier for **1e**. The energy difference between the 90° twisted form and the s-trans form for these two compounds should not be very different.

The aldehydes **1a–h** are all predicted to exist in a planar or close to planar s-trans conformation to the extent of 90% or more at room temperature in the vapor phase. Dipole moment data[31] and spectroscopic data[14,18,20,23,32] are all consistent with a preferred planar s-trans conformation for $\alpha,\beta$-unsaturated aldehydes.

The less stable s-cis conformations of acrolein (**1a**), methacrolein (**1b**), and crotonaldehyde (**1c**) are predicted to be planar, in contrast to the aldehydes **1d–h** where a twisted conformation is predicted to be more stable than the planar one. The largest twist occurs when $R_4$ = Me. The repulsion between the methyl group hydrogens and the carbonyl oxygen is relieved by a significant increase in the tor-

**Table II.** Calculated Conformations and Energies for α,β-Unsaturated Aldehydes and Ketones (see Figure 1)

| Compd | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $\omega_1$, deg | $\omega_2$, deg | $\Delta E(\omega_1 - \omega_2)$, kcal/mol | $-\Delta H°$(exptl), kcal/mol | $\Delta E(90° - \omega_2)$, kcal/mol | $\Delta H^{\ddagger}$(exptl), kcal/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| **1a** | H | H | H | H | 0.0 | 180.0 | 1.64[a] | 1.60[14] | 6.53[a] | 6.64[14] |
| **1b** | H | Me | H | H | 0.0 | 180.0 | 3.06[a] | 3.07[16] | 7.21 | 8.38[16] |
| **1c** | H | H | Me | H | 0.0 | 180.0 | 1.82 | 1.93[16] | 6.97 | 7.44[16] |
| **1d** | H | H | H | Me | 13.4 | 180.0 | 1.34 | | 4.97 | |
| **1e** | H | Me | Me | H | 2.8 | 178.6 | 3.26 | | 6.94 | 6.83[41] |
| **1f** | H | Me | H | Me | 18.1 | 180.0 | 2.65 | | 5.37 | |
| **1g** | H | H | Me | Me | 14.9 | 180.0 | 1.41 | | 5.08 | |
| **1h** | H | Me | Me | Me | 22.2 | 172.9 | 3.06 | | 5.29 | |
| **2a** | Me | H | H | H | 0.0 | 180.0 | 0.56[a] | 0.565 ± 0.052[15] | 5.16 | |
| **2b** | Me | Me | H | H | 0.0 | 180.0 | 1.57 | | 4.88 | |
| **2c** | Me | H | Me | H | 0.0 | 180.0 | 0.71 | 0.585 ± 0.046[15] | 5.44 | |
| **2d** | Me | H | H | Me | 12.9 | 155.1 | −1.74 | | *b* | |
| **2e** | Me | Me | Me | H | 6.9 | 177.6 | 1.70 | | 4.17 | |
| **2f** | Me | Me | H | Me | 34.8 | 142.0 | −1.47 | | *b* | |
| **2g** | Me | H | Me | Me | 18.8 | 151.2 | −1.74 | | *b* | |
| **2h** | Me | Me | Me | Me | 48.9 | 139.7 | −0.60 | | *b* | |

[a] These values were obtained by fitting to experimental data. [b] See text and Figure 2.

sional angle ω (Figure 1). However, the energy difference between the nonplanar and a planar s-cis conformation is in all cases quite small, 0.5 kcal/mol or less. The potential surface in the vicinity of the energy minimum is thus very shallow and large oscillations may be expected. A recent NMR investigation of acrolein in a nematic phase[33] indicated that the s-cis conformation is twisted approximately 45°, which suggests that the compound undergoes very large torsional motions, or that the position of the shallow s-cis minimum may be significantly influenced by intermolecular forces. In the vapor phase a planar s-cis as well as a planar s-trans conformation is observed.[14]

The calculated barriers to rotation around the partial double bond (s-trans → s-cis) are largely determined by the substituent $R_4$. If $R_4$ = H the barrier is quite close (within 0.7 kcal/mol) to that in acrolein (Table II). When $R_4$ = Me the barrier is lowered by about 1.5 kcal/mol due to repulsion between this methyl group and the aldehyde hydrogen, which increases the energy of the planar s-trans conformation. No experimental barriers for compounds where $R_4$ = Me are available.

Our calculations on α,β-unsaturated ketones (**2a–h**) indicate that, predictably, the conformational behavior of these compounds is more sensitive to the substitution pattern at the double bond than was the case for the corresponding aldehydes. The geometry of the most stable conformation is mainly determined by the substituent $R_4$. A methyl group in this position gives strong repulsive interactions with the methyl group attached to the carbonyl group. This repulsion is relieved by significant twisting around the partial double bond. In these cases a twisted s-cis conformation is predicted to be preferred, very strongly in **2d, 2f,** and **2g** and less so in **2h.** When $R_4$ = H, a planar s-trans form is calculated to be most stable (**2a–c** and **2e**).

The available experimental data are mostly of a qualitative nature, but preferred s-cis or twisted s-cis conformations for **2d** and **2f–h** are indicated by spectroscopic[28,29,34,35] and dipole moment[31] studies, while s-trans is preferred for **2a–c** and **2e.** A strong predominance of the s-trans conformer for **2e** is suggested by ir data.[6] The torsional angle (ω) in mesityl oxide (**2h**) has been estimated from Kerr constants to be 38°,[36] significantly larger than our calculated 18.8°. The accuracy of conclusions made from Kerr constants is not high, however, due to the approximations involved. It should also be noted that a twist from 18.8 to 38° in mesityl oxide corresponds to a rather small energy increase, only 0.3 kcal/mol according to our calculations (Figure 2a).

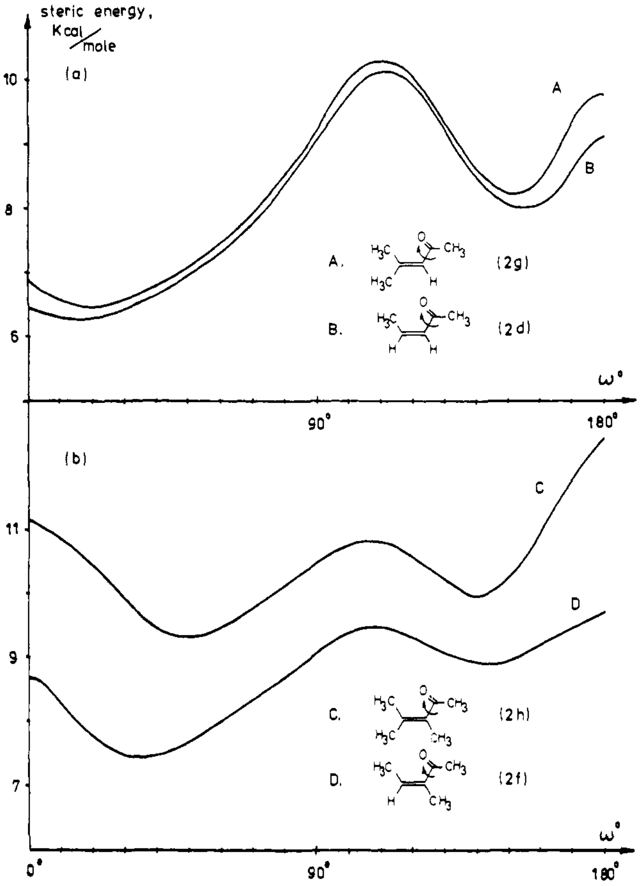

**Figure 2.** Calculated potential curves for compounds **2d** and **2f–h.**

Calculated potential curves for compounds **2d** and **2f–h** are shown in Figure 2. The curves for **2d** and **2g** are similar in shape showing shallow minima at 12.9 and 18.8°, respectively (Figure 2a). The barrier between the lowest energy conformation and the other stable conformation, a twisted s-trans form, is in each case less than 4 kcal/mol. A methyl group in the a position ($R_2$ = Me) changes the calculated potential curves drastically as shown in Figure 2b. The barrier at (approximately) ω = 110° becomes smaller, less than 2 kcal/mol, and in the fully methyl substituted compound (**2h**) the barriers at ω = 0 and 180° are dominating.

## Electronic Transitions

Using the geometries generated by the calculations de-

**Table III.** Calculated and Experimental Ultraviolet Spectra

| Compd | Conformation[a] | Calcd,[b] nm (eV) | $f$ | Sum of Gaussian curves,[c] (nm) | Exptl, nm (eV) | In EtOH $\epsilon$ | Ref |
|---|---|---|---|---|---|---|---|
| **1a** | s-trans | 210.5 (5.89) | 0.45 | 208 | 207 (5.99) | 11 200 | 32 |
| | | 203.5 (6.09) | 0.32 | | | | |
| **1b** | s-trans | 226.2 (5.48) | 0.38 | 214 | 216 (5.74) | 11 000 | 32 |
| | | 201.6 (6.15) | 0.37 | | | | |
| **1c** | s-trans | 217.9 (5.69) | 0.59 | 217 | 218 (5.69) | 17 900 | 32 |
| | | 208.0 (5.96) | 0.16 | | | | |
| **1d** | s-trans | 219.0 (5.66) | 0.57 | 218 | | | |
| | | 207.6 (5.97) | 0.19 | | | | |
| **1e** | $\omega_2 = 178.6°$ | 234.3 (5.29) | 0.43 | 233 | 226 (5.48) | 16 100 | 32 |
| | | 208.7 (5.94) | 0.30 | 210 (sh)[d] | | | |
| **1f** | s-trans | 235.7 (5.26) | 0.42 | 234 | | | |
| | | 208.0 (5.96) | 0.31 | 210 (sh) | | | |
| **1g** | s-trans | 226.2 (5.48) | 0.62 | 226 | 235.5 (5.26) | 11 900 | 32 |
| | | 211.5 (5.86) | 0.12 | | | | |
| **1h** | $\omega_2 = 172.9°$ | 246.4 (5.03) | 0.44 | 246 | 245 (5.06) | 13 000 | 32 |
| | | 215.6 (5.75) | 0.25 | 216 | | | |
| **2a** | s-trans | 208.7 (5.94) | 0.51 | 208 | 208.5 (5.95) | 8 200[e] | 29, 42 |
| | | 200.6 (6.18) | 0.25 | | | | |
| **2a** | s-cis | 223.4 (5.55) | 0.32 | | | | |
| | | 202.5 (6.12) | 0.05 | | | | |
| **2b** | s-trans | 214.5 (5.78) | 0.49 | 214 | 217.8 (5.69) | 10 200 | 28 |
| | | 204.9 (6.05) | 0.25 | | | | |
| **2b** | s-cis | 230.0 (5.39) | 0.34 | | | | |
| | | 209.4 (5.92) | 0.01 | | | | |
| **2c** | s-trans | 214.5 (5.78) | 0.67 | 215 | 220 (5.63) | 11 600[e] | 29, 42 |
| | | 205.2 (6.04) | 0.08 | | | | |
| **2c** | s-cis | 230.8 (5.37) | 0.34 | | | | |
| | | 205.9 (6.02) | 0.04 | | | | |
| **2d** | $\omega_1 = 12.9°$ | 226.6 (5.47) | 0.39 | 227 | 226[f] (5.48) | 8 500 | 7 |
| | | 204.9 (6.05) | 0.03 | | | | |
| **2e** | $\omega_2 = 177.6°$ | 223.0 (5.56) | 0.55 | 222 | 227.9 (5.44) | 12 600 | 28 |
| | | 210.1 (5.90) | 0.18 | | | | |
| **2f** | $\omega_1 = 34.8°$ | 233.0 (5.32) | 0.30 | 233 | 235.5 (5.26) | 4 570 | 43 |
| | | 199.6 (6.21) | 0.08 | 200 | | | |
| **2g** | $\omega_1 = 18.8°$ | 232.6 (5.33) | 0.40 | 233 | 237 (5.23) | 12 700 | 28 |
| | | 206.6 (6.00) | 0.02 | | | | |
| **2h** | $\omega_1 = 48.9°$ | 243.1 (5.10) | 0.21 | 243 | 244.5 (5.07) | 5 300 | 28 |
| | | 191.3 (6.48) | 0.18 | 191 | | | |
| **2h** | $\omega_2 = 139.7°$ | 239.8 (5.17) | 0.26 | | | | |
| | | 190.4 (6.51) | 0.26 | | | | |

[a] If one conformation predominates by more than 90%, only this conformation was considered. [b] The calculated values were corrected for ethanol solvent by −0.40 eV for all transitions. This is the mean difference between absorption maxima in vapor phase and in ethanol solution for a number of $\alpha,\beta$-unsaturated aldehydes and ketones.[44] [c] The band width at half-height was estimated to be 6000 cm$^{-1}$ from the spectrum of mesityl oxide (**2g**).[45] This value was used for all transitions. (See also ref 7.) For **2a–c** and **2h** the sum is taken over a weighted combination of four bands, corresponding to the conformer populations at 25 °C, calculated from Table II. [d] sh = shoulder. [e] In cyclohexane. [f] Estimated from spectrum in hexane ($\lambda_{max}$ 221 nm (5.62 eV)) by subtracting 0.14 eV. This is the difference of the transition energies in hexane and ethanol for the related compound **2g**.[28]

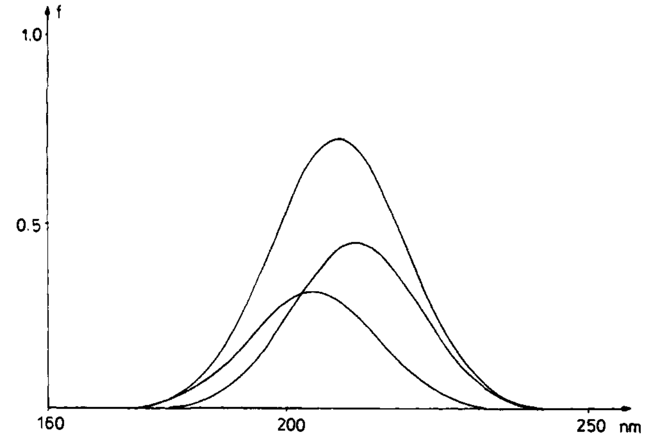

**Figure 3.** Summation of Gaussian curves for acrolein (**1a**).

scribed above, the electronic spectra of compounds **1a–h** and **2a–h** were calculated by the VESCF-CI method. This method has been thoroughly described in previous works.[5,9,11a] Methyl group substitution is accounted for by corrections to the $\pi$-orbital exponents.[9] The configuration interaction included all singly and doubly excited configurations. In the present work only $\pi \rightarrow \pi^*$ transitions were considered.

Calculated and experimental spectra are given in Table III. A point of interest in the calculated spectra is that two transitions are usually predicted to occur in the vicinity of the observed absorption maxima. Earlier VESCF-CI calculations on conjugated carbonyl compounds also showed this quite unexpected (at the time) feature.[11a] Experimental spectra of these compounds normally show only one broad band. However, the lack of symmetry of this band in many spectra suggests that more than one transition may be involved. In some cases the presence of small shoulders on the short wavelength side of the broad band has been observed.[8a] More important, a comparison of optical rotatory dispersion[8a] and circular dichroism[8b] curves of $\alpha,\beta$-unsaturated ketones and structurally related dienes indicate the presence of two close-lying transitions in the former compounds. Since other calculations have predicted that the observed band in enone spectra consists of only a single transition,[37–40a] it is important to clarify this situation. We found that if only singly excited states were included in the configuration interaction, as is the usual case in this type of calculation, only one transition is obtained. Thus with only singly excited configurations, for *trans*-acrolein this calculated value (not corrected for solvent interactions) is 198.8 nm ($f$ = 0.98); the next transition is separated from this one by 35 nm and is nearly forbidden (163.5 nm, $f$ = 0.03). When the doubly excited configurations are included, the transitions are at 197.0 nm ($f$ = 0.45) and 191.0 (0.32). It is thus clear that inclusion of doubly excited configurations is of crucial importance in the calculation of electronic spectra of this class of compounds, and particularly for an understanding of optical rotatory dispersion and circular dichroism spectra.[40b]

If a sum of Gaussian curves is taken to represent the resulting absorption band for the compounds discussed here, a single broad band is in most cases predicted (Figure 3). The predicted values for $\lambda_{\max}$ from such a summation are given in Table III. In a few cases an additional shoulder (**1e** and **1f**) or two separate bands (**1h, 2f,** and **2h**) are predicted. Except for **2f** and **2h,** small changes in parameters or solvent corrections may cause the extra bands and shoulders to overlap the long-wavelength transition. It is therefore uncertain whether or not resolution is to be expected. For compounds **2f** and **2h** the separation is large enough to make the prediction of two separate observable bands more reliable, but in these cases the position of the short wavelength absorption maximum is at or below 200 nm in ethanol, and it may therefore be difficult to observe in practice.

The calculated absorption maxima (Table III) compare favorably with the experimental ones. The difference is less than 0.14 eV in all cases except for compound **1g** where the difference is somewhat larger, 0.22 eV. (The broad bands normally observed lead to uncertainties in the determination of the position of the absorption maximum. It is not unusual that experimental values for the same quantity from different papers differ by several nanometers.) The calculations also show the generally observed decrease in the absorption intensity for a s-cis conformation when compared to a s-trans conformation.

It may be concluded that the geometries and conformations obtained from our mechanical model provide a satisfactory basis for the electronic transitions of the compounds studied in this paper. Our VESCF-CI calculations strongly suggest that the broad uv absorption band observed for $\alpha,\beta$-unsaturated aldehydes and ketones is generally made up of two $\pi \rightarrow \pi^*$ transitions, as predicted earlier,[11a] and as subsequently observed in ORD and CD spectra.[8]

Finally, we conclude that we now have available for the first time a systematic, reasonably accurate, quantitative conformational analysis for acrolein, butenone, and their methylated derivatives.

## References and Notes

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(3) Division of Organic Chemistry, University of Lund, Chemical Center, S-220 07, Lund 7, Sweden.
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