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# ELECTRONIC SPECTRA OF $\alpha,\beta$-UNSATURATED CARBONYL COMPOUNDS—II

## AN EVALUATION OF INCREMENTS CHARACTERISTIC OF STRUCTURAL FEATURES OF $\beta$-OXY-$\alpha,\beta$-UNSATURATED KETONES†

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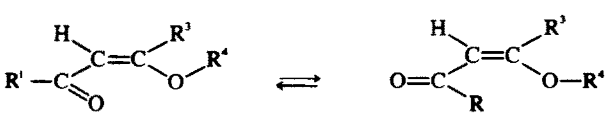
**Abstract**—By comparing UV spectra of $\beta$-alkoxy-$\alpha,\beta$-unsaturated ketones of established steric structure, spectral constants characteristic of the *cis/trans* configuration change and s-*cis*/s-*trans* and O-s-*cis*/O-s-*trans* conformation changes have been evaluated. These are: $\Delta\lambda^{cis}_{trans} = 0$, $\Delta\lambda^{s\text{-}cis}_{s\text{-}trans} = 8$ nm and $\Delta\lambda^{O\text{-}s\text{-}trans}_{O\text{-}s\text{-}cis} = 6$ nm. A comparison of *cis*-s-*cis* enol ethers with the parent enols yielded the increment for the intramolecular ("chelating") H-bond, $\Delta\lambda_{chel} = 24$ nm. The methanol-induced bathochromic shift has been found to depend strongly on s-*cis*/s-*trans* isomerism. The substituent increments have been shown to be dependent on the degree of substitution in the reference molecule. The results obtained have been summarized in a set of spectral increments complementing the basic system of Woodward and the Fiesers.

In a recent paper[1] a new approach to the calculation of the wavelength of the $\pi \rightarrow \pi^*$ absorption max of $\beta$-substituted $\alpha,\beta$-unsaturated aldehydes and ketones has been proposed. This method, which may be viewed as an extension of the Woodward rules,[2,3] takes into account the configuration and conformation of the molecules through a direct comparison of isomers, i.e. without resort to the usual procedure of obtaining the desired conformation and configuration by introducing alkyl substituents or by ring closure. The new approach appears to have a definite advantage, since the alternative route does not permit separation of the contributions of the electronic effect of the alkyl residue introduced and of ring strain from the contribution due to change of configuration and/or conformation.

The UV spectra of $\beta$-alkoxy-$\alpha,\beta$-unsaturated ketones described in the present paper lead to even more unambiguous conclusions than the previously investigated enamino ketones[1] in that they eliminate the problem of the spectral contribution of the intramolecular H-bond unavoidably occurring in the *cis* isomers of the latter group of compounds.

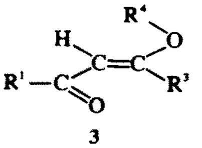
The compounds now under consideration, the general formula of which is $R^1$–CO–$CR^2 = CR^3OR^4$, can be subdivided into two groups: $\beta$-diketone enol ethers ($R^3$ = alkyl) and $\beta$-ketoaldehyde enol ethers ($R^3$ = H). The former can be obtained both as the *cis* (Z) and the *trans* (E) isomers, whereas for the latter it was only possible to synthesize thermodynamically stable *trans* (E) isomers. For both groups two types of conformational isomerism have been observed,[4,5] viz. those due to rotation around the $C_{sp^2} - C_{sp^2}$ and the $C_{sp^2} - O$ single bonds. The rotamer populations are dependent on steric requirements of the substituents $R^1$, $R^2$, $R^3$ and $R^4$. The rotamers, which have been detected by means of IR spectroscopy[4,5] are shown on Charts A + C.



1
ZZE (i.e. *cis*/s-*cis*/O-s-*trans*)

2
ZEE (i.e. *cis*/s-*trans*/O-s-*trans*)

Chart A. The observed conformational isomers of *cis*(Z) $\beta$-diketone enol ethers.[5]



3
EZZ (i.e. *trans*/s-*cis*/O-s-*cis*)

Chart B. The observed conformational isomer of *trans*(E) $\beta$-diketone enol ethers.[5]

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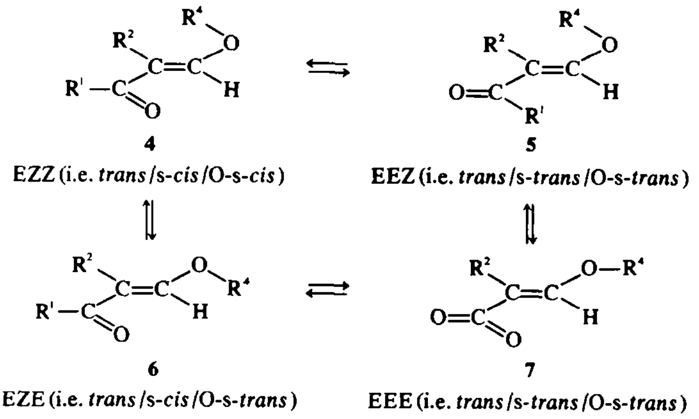


Chart C. The observed conformational isomers of *trans* (E) $\beta$-ketoaldehyde enol ethers.[4]

Table 1. UV spectra ($\pi \rightarrow \pi^*$) of $\beta$-diketone *cis* (Z) and *trans* (E) enol ethers $R^1-\overset{\overset{\Large O}{\|}}{C}-CH=CR^3-OR^4$

| Compound | $R^1$ | $R^3$ | $R^4$ | Configuration | Preferred conformation [a] $Csp^2 - Csp^2$ | $Csp^2 - O$ | $\lambda_{max}^{C_6H_{12}}$, nm obsd | calcd |
|---|---|---|---|---|---|---|---|---|
| 1Z | $CH_3$ | $CH_3$ | $CH_3$ | cis | s-trans > s-cis | O-s-trans [b] | 247 | 248 |
| 1E | | | | trans | s-cis | O-s-cis | 249 | 250 |
| 2Z | $CH_3CH_2$ | $CH_3CH_2$ | $CH_3CH_2$ | cis | s-trans ≉ s-cis | O-s-trans[b] | 249 | |
| 2E | | | | trans | s-cis | O-s-cis | 250 | 250 |
| 3Z | $(CH_3)_2CH$ | $(CH_3)_2CH$ | $CH_3$ | cis | s-cis > s-trans | O-s-trans[b] | 257 | 256 |
| 3E | | | | trans | s-cis | O-s-cis | 251 | 250 |
| 4Z | $CH_3$ | $CH_3$ | $CH_3CH_2$ | cis | s-trans > -s-cis | O-s-trans[b] | 247 | 248 |
| 4E | | | | trans | s-cis | O-s-cis | 249 | 250 |
| 5Z | $CH_3CH_2$ | $CH_3CH_2$ | $CH_3CH_2$ | cis | s-trans ≃ s-cis | O-s-trans[b] | 250 | |
| 5E | | | | trans | s-cis | O-s-cis | 250 | 250 |
| 6Z | $(CH_3)_2CH$ | $(CH_3)_2CH$ | $CH_3CH_2$ | cis | s-cis > s-trans | O-s-trans[b] | 257 | 256 |
| 6E | | | | trans | s-cis | O-s-cis | 252 | 250 |
| 7Z | $CH_3$ | $CH_3$ | $(CH_3)_2CHCH_2$ | cis | s-trans > s-cis | O-s-trans[b] | 248 | 248 |
| 7E | | | | trans | s-cis | O-s-cis | 250 | 250 |
| 8Z | $(CH_3)_3C$ | $CH_3$ | $CH_3$ | cis | s-cis | O-s-trans[b] | 258 | 256 |
| 8E | | | | trans | s-cis | O-s-cis | 250 | 250 |

| Compound | Δ | $\varepsilon_{max}^{C_6H_{12}}$ | $\Delta\lambda_Z^E$ [c] nm | $\lambda_{max}^{CH_3OH}$, nm obsd | calcd | Δ | $\varepsilon_{max}^{CH_3OH}$ | $\Delta\lambda_{C_6H_{12}}^{CH_3OH}$ [d] |
|---|---|---|---|---|---|---|---|---|
| 1Z | +1 | 13250 | +2 | 263 | 264 | +1 | 16200 | 16 |
| 1E | +1 | 13900 | | 257 | 258 | +1 | 13700 | 8 |
| 2Z | | 12000 | +1 | 261 | | | 13500 | 12 |
| 2E | 0 | 13200 | | 259 | 258 | -1 | 14950 | 9 |
| 3Z | -1 | 11950 | -6 | 263 | 264 | +1 | 12580 | 6 |
| 3E | -1 | 14450 | | 260 | 258 | -2 | 15900 | 9 |
| 4Z | +1 | 15900 | +2 | 263 | 264 | +1 | 18700 | 16 |
| 4E | +1 | 16180 | | 257 | 258 | +1 | 18300 | 9 |
| 5Z | | 10600 | 0 | 263 | | | 13500 | 13 |
| 5E | 0 | 12700 | | 259 | 258 | -1 | 14900 | 9 |
| 6Z | -1 | 11300 | -5 | 264 | 264 | 0 | 12650 | 7 |
| 6E | -2 | 14600 | | 261 | 258 | -3 | 17650 | 9 |
| 7Z | 0 | 15600 | +2 | 264 | 264 | 0 | 18600 | 16 |
| 7E | 0 | 14500 | | 259 | 258 | -1 | 16450 | 9 |
| 8Z | -2 | 10100 | -8 | 267 | 264 | -3 | 14400 | 9 |
| 8E | 0 | 14300 | | 258 | 258 | 0 | 11800 | 8 |

[a] Established by means of IR spectroscopy.[5]

[b] Or nonplanar

[c] $\Delta\lambda_Z^E = \lambda_{max}^{C_6H_{12}}(E) - \lambda_{max}^{C_6H_{12}}(Z)$.

[d] $\Delta\lambda_{C_6H_{12}}^{CH_3OH} = \lambda_{max}^{CH_3OH} - \lambda_{max}^{C_6H_{12}}$.

## RESULTS AND DISCUSSION

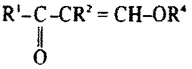
UV spectral data of $\beta$-diketone enol ethers, $\beta$-ketoaldehyde enol ethers and $\beta$-diketone enols are presented in Tables 1, 2-3, respectively.

*Breaking down of $\pi \rightarrow \pi^*$ spectral shifts into structural components*

Let us consider first the *cis* (Z) and *trans* (E) $\beta$-diketone enol ethers. In order to eliminate the problem of spectral perturbations caused by specific solvent-solute interactions spectra of solutions in cyclohexane will be discussed.

As shown by IR spectra[5] the *cis* (Z) isomers of compounds containing $R^1 = Me$, i.e. **1Z**, **4Z** and **7Z** exist predominantly in the s-*trans*[†]/O-s-*trans*[‡] conformation II

Table 2. UV spectra ($\pi \rightarrow \pi^*$) of $\beta$-ketoaldehyde *trans* (E) enol ethers



$R^1\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}CR^2 = CH\text{–}OR^4$

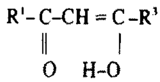
| Compound | $R^1$ | $R^2$ | $R^4$ | Preferred conformation[a] Csp$^2$ - Csp$^2$ | Csp$^2$ - O |
|---|---|---|---|---|---|
| 9 | $CH_3$ | H | $CH_3$ | s-cis ≈ s-trans | O-s-cis > O-s-trans |
| 10 | $(CH_3)_2CH$ | H | $CH_3$ | s-cis > s-trans | O-s-cis > O-s-trans |
| 11 | $(CH_3)_2CH$ | H | $(CH_3)_2CH$ | s-cis > s-trans | O-s-trans > O-s-cis |
| 12 | $(CH_3)_3C$ | H | $CH_3$ | s-cis | O-s-cis > O-s-trans |
| 13 | $(CH_3)_3C$ | H | $(CH_3)_2CH$ | s-cis | O-s-trans > O-s-cis |
| 14 | $(CH_3)_3C$ | H | $(CH_3)_3C$ | s-cis | O-s-trans |
| 15 | $CH_3CH_2$ | $CH_3$ | $CH_3$ | s-trans | O-s-trans |
| 16 | $CH_3CH_2$ | $CH_3$ | $(CH_3)_2CH$ | s-trans | O-s-trans |

| Compound | $\lambda_{max}^{C_6H_{12}}$, nm obsd | calcd | $\Delta$ | $\varepsilon_{max}^{C_6H_{12}}$ | $\lambda_{max}^{CH_3OH}$, nm obsd | calcd | $\Delta$ | $\Delta\lambda_{C_6H_{12}}^{CH_3OH}$ [b] |
|---|---|---|---|---|---|---|---|---|
| 9 | 237 | | | 13450 | 246 | | | 11 |
| 10 | 242 | 246 | +4 | 12900 | 249 | 254 | +5 | 7 |
| 11 | 252 | 252 | 0 | | 256 | 260 | -4 | 4 |
| 12 | 246 | 246 | 0 | 9750 | 255 | 254 | -1 | 9 |
| 13 | 253 | 252 | -1 | 11000 | 262 | 260 | -2 | 9 |
| 14 | 256 | 252 | -4 | 13500 | 265 | 260 | -5 | 9 |
| 15 | 247 | 248 | +1 | 15500 | 256 | 264 | +8 | 9 |
| 16 | 250 | 248 | -2 | 16150 | 259 | 264 | +5 | 9 |

[a] Established by means of IR spectroscopy.[4]

[b] $\Delta\lambda_{C_6H_{12}}^{CH_3OH} = \lambda_{max}^{CH_3OH} - \lambda_{max}^{C_6H_{12}}$.

Table 3. UV spectra of $\beta$-diketone enols



$R^1\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}CH = \underset{\underset{\displaystyle H\text{–}O}{|}}{C}\text{–}R^3$

| Compound | $R^1$ | $R^3$ | $\lambda_{max}^{C_6H_{12}}$, nm obsd | calcd | $\Delta$ | $\varepsilon_{max}^{C_6H_2}$ | $\lambda_{max}^{CH_3OH}$, nm obsd | calcd | $\Delta$ | $\varepsilon_{max}^{CH_3OH}$ | $\Delta\lambda_{C_6H_{12}}^{CH_3OH}$ [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17 | $CH_3$ | $CH_3$ | 273 | 274 | +1 | - | 275 | 275 | 0 | - | 2 |
| 18 | $CH_3CH_2$ | $CH_3CH_2$ | 275 | 274 | -1 | - | 275 | 275 | 0 | - | 0 |
| 19 | $(CH_3)_2CH$ | $(CH_3)_2CH$ | 275 | 274 | -1 | 11800 | 276 | 275 | -1 | 11000 | 1 |
| 20 | $(CH_3)_3C$ | $CH_3$ | 275 | 274 | -1 | 11800 | 276 | 275 | -1 | 10500 | 1 |

[a] $\Delta\lambda_{C_6H_{12}}^{CH_3OH} = \lambda_{max}^{CH_3OH} - \lambda_{max}^{C_6H_{12}}$

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[†] Some admixture of s-*cis* conformer, which has a lower value, should be insignificant, indeed, measurements on mixtures of isomers having similar spectral characteristics prepared on purpose showed the absorption max of the main component to be practically unaffected by small admixtures.[1]

[‡] As mentioned in Ref. 5, the =C-OR[4] fragment may deviate from planarity.

while their *trans* (E) isomers have exclusively the s-*cis*/O-s-*cis* structure III. Hence, assuming that structural effects on the position of the $\pi \rightarrow \pi^*$ absorption max are additive, the observed λ max shift accompanying Z→E isomerisation can be expressed as a sum of three components in the following way:

$$\lambda_{\mathrm{EZZ}} - \lambda_{\mathrm{ZEE}} = \Delta\lambda^{trans/\text{s-}cis/\text{O-s-}cis}_{cis/\text{s-}trans/\text{O-s-}trans} = \Delta\lambda^{trans}_{cis} + \Delta\lambda^{\text{s-}cis}_{\text{s-}trans} + \Delta\lambda^{\text{O-s-}cis}_{\text{O-s-}trans} = 2\,\text{nm}^{\dagger} \qquad (1)$$

The first and the third components of eqn (1) can be eliminated by considering compounds **3**, **6** and **8** containing bulky $R^1$ substituents. Their *cis* (Z) isomers exist predominantly (**3Z** and **6Z**) or exclusively (**8Z**) in the s-*cis*/O-s-*trans* conformation I while for the *trans* (E) isomers the conformation is again exclusively s-*cis*/O-s-*cis* III. Therefore

$$\lambda_{\mathrm{EZZ}} - \lambda_{\mathrm{ZZE}} = \Delta\lambda^{trans/\text{s-}cis/\text{O-s-}cis}_{cis/\text{s-}cis/\text{O-s-}trans} = \Delta\lambda^{trans}_{cis} + \Delta\lambda^{\text{O-s-}cis}_{\text{O-s-}trans} \cong -6\,\text{nm}^{\ddagger} \qquad (2)$$

By subtracting eqn (2) from the eqn (1) the effect of pure s-*cis*→s-*trans* conformational change on the $\lambda_{\max}$ is obtained:

$$\text{eqn (1)} - \text{eqn (2)} \Rightarrow \Delta\lambda^{\text{s-}cis}_{\text{s-}trans} \cong 8\,\text{nm}.$$

It should be noted that within this group of compounds the solvatochromic effects are clearly different for the s-*cis* and s-*trans* conformers, $\Delta\lambda^{\mathrm{MeOH}}_{\mathrm{C_6H_{12}}}$ amounting to 6 ÷ 9 nm mean value 8 nm for the former and 16 nm for the latter (Table 1); in the case of a mixture containing appreciable amounts of both conformers (2Z and 5Z), $\Delta\lambda^{\mathrm{MeOH}}_{\mathrm{C_6H_{12}}}$ has intermediate values (12 and 13 nm, respectively). This behaviour seems to be significant when explaining the fact that Woodward and the Fiesers' rules give a relatively good agreement with experiment though they do not distinguish conformations. It follows from the above data that the difference between the solvatochromic effects of the two conformers amounts to 8 nm, i.e. it has the same absolute value as the $\Delta\lambda^{\text{s-}cis}_{\text{s-}trans}$ has but is of the opposite sign. Since the above mentioned rules were formulated for alcoholic solutions, the apparent independence of the Woodward-Fiesers' increments of conformation may be accounted for by the compensation of the conformational effect, $\Delta\lambda^{\text{s-}cis}_{\text{s-}trans}$, and by the solvatochromic effect, $\Delta\lambda^{\mathrm{MeOH}}_{\mathrm{C_6H_{12}}}$. The constancy of the solvent increments postulated by these rules is thus questionable.

Theoretical calculations by Favini *et al.*[6] led to larger $\Delta\lambda^{\mathrm{MeOH}}_{\mathrm{C_6H_{14}}}$ values for the s-*trans* conformation of β-chlorosubstituted enones than for the s-*cis* one—a tendency qualitatively in agreement with our data. However, the sign of the predicted[6] methanol-induced shift for the s-*cis* conformation was negative which has never previously been observed for enones.

Returning to the evaluation of the remaining two increments, viz. $\Delta\lambda^{trans}_{cis}$ and $\Delta\lambda^{\text{O-s-}cis}_{\text{O-s-}trans}$, we will use the data on β-ketoaldehyde enol ethers presented in Table 2. As established by IR measurements[4] the increase of the bulkiness of the substituent $R^4$ in **11** vs **10** or in **13** nad **14** vs **12** results in an equilibrium shift towards the O-s-*trans* conformation, IV→VI. The accompanying batochromic shift amounting to 7–10 nm (average value 9 nm) is composed of the conformational factor $\Delta\lambda^{\text{O-s-}trans}_{\text{O-s-}cis} = -\Delta\lambda^{\text{O-s-}cis}_{\text{O-s-}trans}$ to be found and of the electronic effect of the substituent $R^4$. The latter can be established by comparing compounds **15** and **16** (both s-*trans*[4]) in which the additional alkyl substituent $R^2$ forces the $OR^4$ fragment to occupy the O-s-*trans* position (structure VII) independently of the size of $R^4$. The comparison yields 3 nm for the electronic effect of the change of $R^4$ = Me for i-Pr. Consequently, the average effect of the O-s-*trans* → O-s-*cis* conformational change, $\Delta\lambda^{\text{O-s-}cis}_{\text{O-s-}trans}$, approximately equals − 6 nm. By substitution of this value into eqn (2) $\Delta\lambda^{trans}_{cis} = 0$ is obtained; in other words, the absorption maximum does not depend on configuration. This remarkable result contradicts the estimates made by Ostercamp[7] and Kashima *et al.*[8] based on oversimplified schemes§ concerning mainly amino derivatives of β-dicarbonyl compounds. It also disagrees with the results of quantum-chemical calculations by Fueno and Yamaguchi[9] and Favini *et al.*[6] On the other hand, the result is in harmony with experimental data obtained by Bienvenue[10] on non functionalized α,β-unsaturated ketones and with their β-amino derivatives.[1] Thus, the independence of the $\pi \rightarrow \pi^*$ absorption wavelength of the configuration of α,β-unsaturated carbonyl compounds seems to be a part of a general tendency.

### *Effect on intramolecular H-bonding*

The enols of β-diketones have the *cis*/s-*cis*/O-s-*cis* structure stabilized by intramolecular ("chelating") H-bonding. In order to estimate the effect of chelation on the UV spectrum the *cis*/s-*cis* enol ethers **3Z**, **6Z** and **8Z** (structure I) will be compared with related enols **19** and **20**.

The average difference of 18 nm thus obtained must be corrected for the conformation of the =C–$OR^4$ fragment which is O-s-*trans* in the ethers. For the hypothetical *cis*/s-*cis*/O-s-*cis* the absorption max should be hypsochromically shifted by $\Delta\lambda^{\text{O-s-}trans}_{\text{O-s-}cis} = 6\,\text{nm}$, i.e. the total difference accounting for the intramolecular H–bond ($\Delta\lambda_{\mathrm{chel}}$) should amount to 24 nm.

### *Substituent effects*

"True" substituent increments not affected by possible changes of conformation can only be evaluated by comparing homologues of exactly the same steric structure. As will be shown below, this necessary condition is, however, not sufficient. For example, **8E** and **12** yield 4 nm as the increment of the Me group ($R^3$ = Me) while 12 nm is obtained if 2,2-dimethylpent-4-en-3-one[11] is compared with *cis* and *trans* 2,2-dimethylhex-4-en-3-ones[10] (Chart D). Similarly, 2,2-dimethylpent-4-en-3-one and **12** yield 36 nm for the O-s-*cis* β-OMe substituent whereas 28 nm results from the alternative comparison of the *cis* (Z) 2,2-dimethylhex-4-en-3-one with **8E**. No doubt, a similar situation would be encountered with the increment of the O-s-*trans* β-OMe group amounting to 36 nm if a suitable reference for an alternative comparison were available.

It follows from the above that substitution on unsaturated systems already substituted has a less pronounced spectral effect than on non-substituted ones. This behaviour finds an explanation in a partial "saturation" of the π-electron system of the absorbing group by the first substituent, the chromophore being thus less susceptible to the influence of the second auxochrome. In addition, steric interaction between substituents may result in deformations weakening the conjugation, thereby contributing to the decrease of the batochromic shift.

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†This value is identical in all the cases investigated (Table 1).

‡Mean from three experimental values (Table 1).

§For a detailed critique (see Ref. 4).

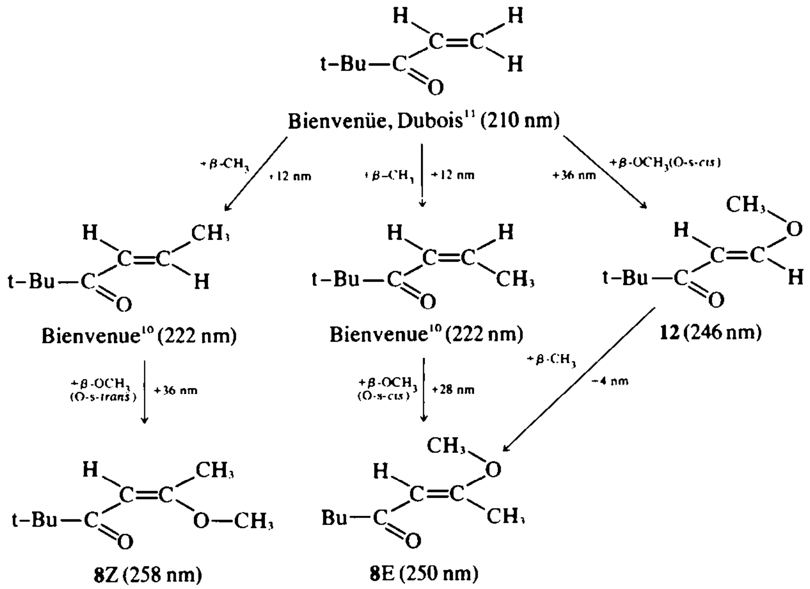

Chart D. Evaluating of the substituent increments.

## CONCLUSION

In the light of the above considerations it appears that it would be almost impossible to develop a general system of substituent increments which would be free of self-contradictory elements. Reliable regularities can only be expected for series of closely related compounds.

For β-hydroxy and β-alkoxy-α,β-unsaturated ketones we tentatively propose the following set of increments related to structure elements:

| Element | Increment (nm) |
|---|---|
| Parent value (s-*trans*/O-s-*cis* structure in cyclohexane) | 238† |
| s-*cis* conformation | 8 |
| O-s-*trans* conformation | 6 |
| β-alkyl substituent | 4 |
| α-alkyl substituent | 4 |
| "Chelating" H-bond | 24 |
| Methanol correction (for s-*cis* structure) | 8 |
| Methanol correction (for s-*trans* structure) | 16 |
| Methanol correction (for enols) | 1 |

†This value follows from our system but is also coinciding with that experimentally found for dimedone methyl ether of the same s-*trans*/O-s-*cis* structure.

The self-consisting of the system is illustrated by the rather small differences Δ between calculated and experimental data indicated in Tables 1–3.

## EXPERIMENTAL

Syntheses of β-diketone enol ethers 1Z–8Z and 1E–8E and of all the β-ketoaldehyde enol ethers discussed except **16** have been described in previous papers.[4,5]

1 - *Isopropoxy* - 2 - *methylpent* - 1 - *en* - *on* (**16**) was obtained by the method analogous to that of Seifert and Schinz.[12] In a flask fitted with a reflux condenser and water separator were placed: 1-hydroxy 2-methylpent - 1 - en - 3 - on (obtained from diethylketone, ethylformate and sodium), equimolar amount of 2-propanol, catalytic amount of *p*-toluenesulphonic acid and a large excess of benzene. The mixture was boiled for 24 hr while water was removed by azeotropic distillation. The mixture was then washed with $NaHCO_3$aq and worked up in usual manner. Vacuum distillation yielded **16** b.p. 44–45°/0·3 mm Hg. (Found: C, 69·25; H, 10·57; Calc. for $CgH_{16}O_2$: C, 69·19; H, 10·32%); NMR (ppm, in $CCl_4$): 1·01 (t, 3H), 1·31 (d, 6H), 1·63 (s, 3H), 2·47 (q, 2H), 4·28 (spt, 1H), 7·45 (s, 1H), IR ($cm^{-1}$ in $C_2Cl_4$): 1693 ($\nu_{C=O}$, s-*cis*), 1665 ($\nu_{C=O}$, s-*trans*) 1644 ($\nu_{C=C}$, s-*trans*), 1641 ($\nu_{C=C}$, s-*cis*).

UV spectra were recorded on Unicam SP-700 and Beckman ACTA MVI spectrophotometers. NMR spectrum was run on a Varian EM360 instrument. IR spectrum was recorded on a Beckman IR-4290 spectrometer. The substances investigated were freshly distilled or sublimed before the measurements, middle fraction being taken. Commercial "for spectroscopy" solvents were used.

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