Alkyl-substituent Effects on the $n \rightarrow \pi^*$ Transition of Some *trans*-Enones in Hexane

By J. E. DUBOIS,* A. BIENVENUE, and M. CHASTRETTE

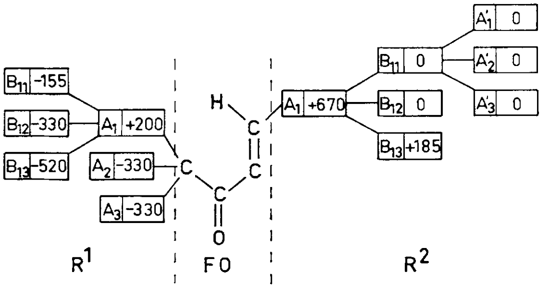
[*Laboratoire de Chimie Organique Physique* (*Associé au C.N.R.S.*), 1, *rue Guy de la Brosse, Paris* 5^e^, *France*]

IN conjugated systems, all alkyl substituents are generally considered to have identical effects upon spectral properties.[1] Work in this laboratory on the $n \rightarrow \pi^*$ transition of saturated ketones has shown that this transition is very sensitive ($\Delta\nu$ about 3800 cm.$^{-1}$) to the nature of the two alkyl groups.[2a] We now show that $\alpha\beta$-unsaturated ketones are similarly affected. By changing the groups R^1 to R^4 in $R^1\cdot CO\cdot CR^3{=}CR^2R^4$ we have distinguished the effects of isolated groups and we hope eventually to be able to estimate interaction effects. We present here results concerning the variation of R^1 and R^2, where R^2 is *trans* with respect to the carbonyl group.

The effect of replacing an ethyl group at R^1 by t-butyl in the series of vinylic ketones $R^1COCH{=}CH_2$ (1—7 in the Table) on the *R*-band,[3] is of the order of 850 cm.$^{-1}$. Furthermore, the frequencies decrease in the following order for change of R^1: Et, Me, Pr, Pr^i, Bu^s, Bu^i, Bu^t. This order is significantly different from that obtained for saturated ketones.[2b]

Finally, the results for the enones 1—5, 8—13 show clearly that the effects of R^1 are independent of the existence or of the nature of substitutents at R^2, *e.g.* the difference between the frequencies of $MeCOCH{=}CHR^2$ and $Bu^tCOCH{=}CHR^2$ is 480 cm.$^{-1}$, a value close to the difference between $MeCOCH{=}CH_2$ and $Bu^tCOCH{=}CH_2$ (610 cm.$^{-1}$).

We have demonstrated an empirical relationship between the structure of the substituents and the frequency of the $n \rightarrow \pi^*$ transition. This relates the position of the *R*-band to the description of the substituents R^1 and R^2 in terms of the Darc system.[4] The position of the enone band is calculated by means of the equation: $\nu = \nu_0 + \sum_i \Delta\nu_i$, where ν_0 is the value in cm.$^{-1}$ for the reference compound, methylvinyl ketone. Values of $\Delta\nu_i$ determined for each position where a carbon atom may exist are shown in a topological diagram (Figure). These results were obtained from a larger mass of data (R^1 ranges from methyl to tetramethylpropyl), and R^2 from H to Bu^t or neo-pentyl). The precision of this correlation is excellent: the mean error



FIGURE

Topological diagram

(The contributions $\Delta\nu_i$ are given in cm.$^{-1}$; ν_0 = 30040 cm.$^{-1}$. In constructing the net we give the lowest index to the most substituted position. The other occupied positions take the lowest index values available. For example, A_3 can only be occupied if A_1 and A_2 are already filled. FO is the focus in the Darc system.)

R-Bands for trans-*enones* $R^1COCH{=}CHR^2$ *in hexane*
(Values in parentheses calculated by means of equation 1)

	R^1	R^2	ν(cm.$^{-1}$)
1	Me	H	30100 (30040)
2	Et	H	30340 (30420)
3	Pr	H	30030 (30095)
4	Pr^i	H	29870 (29910)
5	Bu^t	H	29490 (29580)
6	Bu^i	H	29730 (29765)
7	Bu^s	H	29810 (29755)
8	Me	Me	30770 (30710)
9	Me	Bu^i	30670 (30710)
10	Me	Bu^t	30890 (30895)
11	Bu^t	Me	30250 (30250)
12	Bu^t	Bu^i	30220 (30250)
13	Bu^t	Bu^t	30420 (30435)

between the calculated and experimental values is 50 cm.$^{-1}$, the maximum error 100 cm.$^{-1}$ and the standard deviation 57 cm.$^{-1}$. The eight parameters given in the Figure, of which three are identical, are sufficient to account for these results and should, theoretically, allow us to calculate the position of the $n \rightarrow \pi^*$ transition for 182 compounds for which the effects of R^1 and R^2 can be calculated from the contributions presented in the Figure. For some acyclic and cyclic compounds[5] a mean value of 6 mμ was calculated for the contribution of R^2: in our treatment it varies from 7·3 to 9·3 mμ.

The relationship determined here gives a better fit than one the using the empirical substituent constants, either polar σ^* [6] or steric $E_{\mathrm{S}}^{\mathrm{C}}$, [7] or any linear combination of these two (standard errors are 253, 235, and 103 cm.$^{-1}$ respectively). $E_{\mathrm{S}}^{\mathrm{C}}$ values are preferable to Taft's E_{S} values because they do not include hyperconjugative contributions. The equation, taken in conjunction with another related to the $\pi \rightarrow \pi^*$ transition of the same compounds,[8] should lead to an easy method for the identification of these compounds. Above all, they form an indispensable quantitative reference for the M.O. calculations of alkyl-substituent effects on spectral properties. Although inductive and mesomeric effects have already been considered,[9] and the replacement of a hydrogen atom by a methyl group has been the subject of different treatments,[10] this problem has yet to be resolved.

(*Received, February 28th*, 1968; *Com.* 245.)

---

[1] See for example, H. H. Jaffé and M. Orchin, "Theory and Applications of UV Spectroscopy", J. Wiley, New York, 1962, pp. 207—217.

[2] (a) From the frequencies observed for acetone (36050 cm.$^{-1}$) and ditriptylketone (32200 cm.$^{-1}$) in hexane (A. Barbi, personal communication); (b) J. E. Dubois and P. Marconi, *Compt. Rend.*, 1956, **243**, 138; P. Maroni, *Ann. Chim. (France)*, 1957, **13**, 757.

[3] A. Burawoy, *J. Chem. Soc.*, 1939, 1177; *ibid.*, 1941, 20.

[4] J. E. Dubois, D. Laurent, and H. Viellard, *Compt. Rend.*, 1966, **263** (*c*), 764; J. E. Dubois and H. Viellard, *Bull. Soc. chim. France*, in the press.

[5] R. C. Cookson and H. Dandegaonker, *J. Chem. Soc.*, 1955, 1651.

[6] R. W. Taft, jun., in "Steric Effects in Organic Chemistry", ed. M. S. Newman, J. Wiley, New York, 1956.

[7] C. K. Hancock, E. A. Meyers, and B. J. Yager, *J. Amer. Chem. Soc.*, 1961, **83**, 4211.

[8] J. E. Dubois and A. Bienvenüe, to be published.

[9] J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules", Methuen, London, 1963.

[10] (a) R. Luft and J. Baso, *Compt. Rend.*, 1967, **265**, *c*, 980; (b) N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, 1965, **87**, 2081.