Structural Effects on the Carbonyl Frequency of Saturated Aliphatic Ketones

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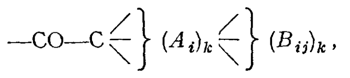
WE have shown,[1,2] that the carbonyl frequency $\nu_{C=O}$ of saturated aliphatic ketones in the gas phase is a function of the different positions of the carbonyl environment (we call this a frequency–topology relationship). Other authors have attempted to correlate this frequency with reactivity parameters such as Taft's σ^*,[3] or E_S.[4] It is our intention to specify the range of applicability of such frequency–reactivity correlations and to show that these frequencies are best described by the topology relationship.

Our study is based on values for 28 ketones, five of which are αα′-hexasubstituted, in the gas phase; the carbonyl environment is limited to the A_i and B_{ij} substituents [this notation comes from the topological diagram of a ketone[5]:



$$\text{—CO—C}\Big\langle\Big\}\,(A_i)_k\Big\langle\Big\}\,(B_{ij})_k,$$

with $k = 1$ or 2, corresponding to each alkyl group].

We have examined several correlations between $\nu_{C=O}$ and the different polar, steric, or hyperconjugative parameters or linear combinations thereof. The best are those which employ the sum of polar and steric parameters (equations 1 and 2:† the first uses Taft's E_S and the second Hancock's[6] E_S^C steric parameters).

$$\nu^{\text{gas}}_{C=O} = 1741 + 22\,\Sigma\sigma^* + 4\Sigma E_S \qquad (1)$$

$$\nu^{\text{gas}}_{C=O} = 1741 + 7\,\Sigma\sigma^* + 4{\cdot}4\Sigma E_S^C \qquad (2)$$

However, these relationships apply only to ketones which are not αα′-hexasubstituted (see Figure a), and we observe that for 23 such ketones involving 11 different groups, 22 values of σ^* and E_S (or E_S^C) are required. Furthermore, systematic deviations are found for several alkyl groups, both in solution and in the gas phase. Ketones involving neopentyl and tetramethylpropyl groups are seen to deviate from the best line (Figure a). Thus, in their present form, these frequency–structure correlations do not permit accurate $\nu_{C=O}$ prediction. To improve the calculation, it would be necessary to add correction terms taking account of interactions inside and between the alkyl groups.

Even so, equations 1 and 2, while equally accurate, give quite different weights to the polar

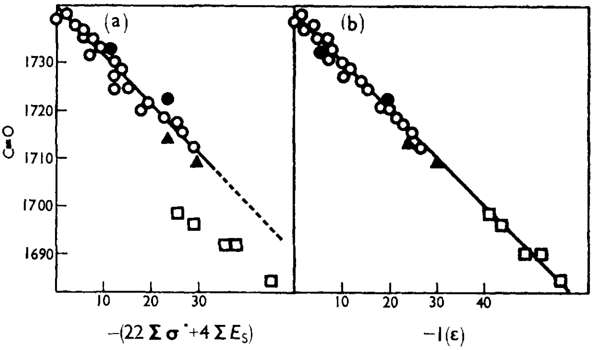


FIGURE. (a) *Frequency–structure correlation;*
(b) *Frequency–topology correlation.*

○ values given in ref. 1; the others are given in ref. 2.

● and ▲ : ketones with one neopentyl or one triptyl group.

□ αα′-hexasubstituted ketones.

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† The correlation coefficients for both equations are: 0·98. Mean and maximum deviations are 1·27 and 4·7 cm.$^{-1}$, in equation (1); 1·26 and 4·3 cm.$^{-1}$ in (2). Standard deviations for polar and steric contributions are 4·5 and 0·5 cm.$^{-1}$ in equation (1); 6 and 0·5 in (2).

contribution; it seems reasonable to ask whether such frequency–structure correlations facilitate the understanding of structural effects (see ref. 7). At best, one can say that they show a general tendency of $\nu_{C=O}$ to be correlated with reactivity parameters.

We obtain more accurate results[1,2] with the frequency-topology relationship (equation 3),‡ as shown in Figure b.

$$\nu^{\text{gas}}_{C=O} = 1740 + I(\varepsilon) \qquad (3)$$

with $I(\varepsilon) =$

$$-\sum_{k=1}^{2}[(A_1)_k + 4(A_2)_k + 9(A_3)_k + 2{\cdot}5\sum_{i=1}^{3}(B_{i1})_k + 2(B_{12})_k + 6{\cdot}5(A_3)_k{\cdot}(B_{13})_k] - 13(A_3)_1{\cdot}(A_3)_2$$

The two terms $(A_3)_1{\cdot}(A_3)_2$ and $A_3{\cdot}B_{13}$ (the latter occurs in a tetramethylpropyl group) take account of interaction between substituents; $I(\varepsilon)$, the environment contribution, is a specific parameter of a ketone.

This relationship (equation 3) requires the knowledge of only eight parameters (one of which, the B_{13} contribution, is found to be zero). It is expected to apply to a much wider range of ketones. As it is, we have found that the carbonyl frequency of 66 ketones in carbon tetrachloride solution could be correlated with this $I(\varepsilon)$ environment contribution.[8]

It seems likely that this approach offers a more economical method of dealing with the total effects of alkyl substituents on molecular properties than σ^* and E_S treatments. We are currently studying its application to other systems.

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‡ The parameters: −1, −4, −9, −2·5, −2, 0·0 (B_{13} contribution), −6·5, −13 (in cm.$^{-1}$) were obtained by computing the carbonyl frequency against a linear combination of the different topological elements A_i, B_{ij} which have the value 0 (if the corresponding position is not occupied by a carbon atom) or unity (occupied). The contributions B_{22}, B_{23}, B_{32}, and B_{33} are as yet undetermined; those of the three B_{i1} were found to be the same at ±0·5 cm.$^{-1}$ (see ref. 9).

[1] J. E. Dubois and A. Massat, *Compt. rend.*, 1967, **265**, *B*, 757.

[2] J. E. Dubois, *et al.*, to be published.

[3] H. W. Thompson and D. A. Jameson, *Spectrochim. Acta*, 1958, **13**, 236; C. N. R. Rao, G. K. Goldman, and C. Lurie, *J. Phys. Chem.*, 1959, **63**, 1311.

[4] K. J. Morgan and N. Unwin, *J. Chem. Soc.* (*B*), 1967, 1336.

[5] J. E. Dubois and H. Viellard, *Bull. Soc. Chim. France*, 1968, pp. 900, 905, and 913.

[6] C. K. Hancock, *J. Amer. Chem. Soc.*, 1961, **83**, 4211.

[7] C. D. Ritchie and W. F. Sager in "Progress in Physical Organic Chemistry", Vol. II; ed. S. G. Cohen, A. Streitwieser, and R. W. Taft, Interscience, New York, 1964, p. 323.

[8] J. E. Dubois, A. Massat, and Ph. Guillaume, *J. Chim. phys.*, 1968, **65**, 729.

[9] J. E. Dubois, D. Laurent, and H. Viellard, *Compt. rend.*, 1967, **264**, *C*, 1019.