Theoretical interpretation of substituent effect on C = O stretching vibration
of s-*trans* and s-*cis* conformation of α,β-unsaturated carbonyl compounds

[a]A. PERJÉSSY and [b]R. PONEC

[a]*Department of Organic Chemistry, Faculty of Natural Sciences,*
Komenský University, CS-842 15 Bratislava

[b]*Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences,*
CS-165 02 Prague

The transmission of the substituent effect in several series of α,β-unsaturated aromatic compounds was analyzed on the basis of SCF-LCI perturbation theory. The proposed approach permits not only to calculate theoretically the ϱ constants of Hammett type correlations between carbonyl stretching frequencies and substituent constants σ, but also to assign the actual conformation of α,β-unsaturated carbonyl compounds.


Анализирован перенос влияния заместителя в нескольких рядах α,β--ненасыщенных ароматических соединений на основе теории возмущений SCF-LCI. Предлагаемый подход позволяет не только теоретически вычислить величины констант ϱ в соотношениях типа Гамметтовских между колебательными частотами карбонильной группы и константой заместителя σ, но также и определить истинную конформацию α,β--ненасыщенных карбонильных соединений.

A number of papers [1—5] were devoted to the theoretical investigation of the Hammett equation from the point of view of the perturbation theory of substituent effect.

Recently [6] the simple HMO approach was used to interpret the ϱ constants of the Hammett type $v(C = O)$ *vs.* σ correlations for a number of series of unsaturated carbonyl compounds. The HMO bond-atom polarizabilities as the theoretical

measure of ϱ constants correlated significantly with experimental ϱ values in a series including rather different structural types. It was shown that the proposed approach can be used to predict the ϱ constants as well as the corresponding transmitting factors for series of carbonyl compounds.
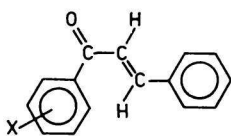
The applicability of the simple HMO approach has, however, some inherent limitations arising from the neglect of electron repulsion in the HMO theory. Thus,
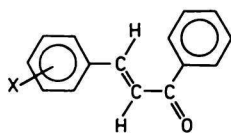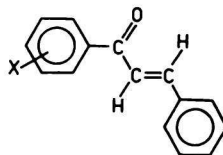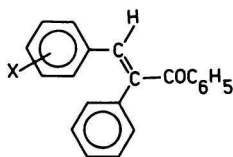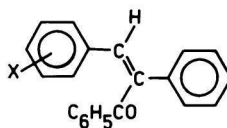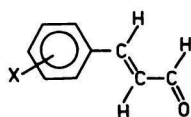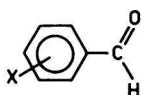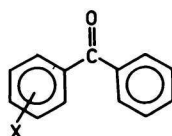

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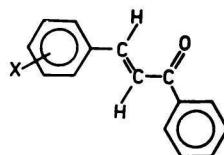
II

III

IV

V

VI

VII

VIII

IX

for example, it is not possible to account for the differences in the substituent effect transmission between the pair of s-*cis* and s-*trans* conformations in α,β-unsaturated carbonyl compounds.

The aim of this paper was to investigate on the basis of recently proposed SCF-LCI perturbation theory of substituent effect [3, 5] just these subtle effects.

The following series of compounds were investigated: (*E*)-s-*trans*-1-phenyl-3--(X-phenyl)propenones (*I*), (*E*)-s-*cis*-1-phenyl-3-(X-phenyl)propenones (*II*), (*E*)--s-*trans*-1-(X-phenyl)-3-phenylpropenones (*III*), (*E*)-s-*cis*-1-(X-phenyl)-3-phenylpropenones (*IV*), (*E*)-1,2-diphenyl-3-(X-phenyl)propenones (*V*), (*Z*)-1,2--diphenyl-3-(X-phenyl)propenones (*VI*), and (*E*)-s-*trans*-3-(X-phenyl)propenals (*VII*). For the sake of comparison substituted benzaldehydes (*VIII*) and diphenylketones (*IX*) were also included in this study.

Experimental

The carbonyl stretching frequencies of the series *I—IX* measured in dilute solutions of CCl_4 were correlated with "well-characterized" substituent constants taken from collection of *Hansch* and *Leo* [7].

The $\tilde{v}(C=O)$ values of the following compounds were included into the correlations: For series *I* and *II*, X = 4-NH$_2$, 4-OCH$_3$, 4-CH$_3$, 3,4-O$_2$CH$_2$, H, 4-F, 4-Cl, 3-Cl, 4-CN, 3-NO$_2$ taken from [8] and X = 3-NCS, 4-NCS taken from [9]. For series *III* and *IV*, X = 4-OCH$_3$, 4-CH$_3$, 4-F, 3-OCH$_3$, 4-Cl, 4-Br, 3-Cl, 3-Br, 3-NO$_2$, 4-NO$_2$, H taken from [8] and X = 3-NCS, 4-NCS taken from [10]. For series *V* and *VI*, X = 4-OCH$_3$, 4-CH$_3$, 4-C$_6$H$_5$, 4-F, H, 4-Cl, 4-Br, 4-NO$_2$ taken from [11]. For series *VII*, X = 4-N(CH$_3$)$_2$, 4-OCH$_3$, 4-CH$_3$, 4-Cl, 3-Cl, 3-Br, 3-NO$_2$, 4-NO$_2$ taken from [12], X = 3-OCH$_3$, 4-Br, 3-F taken from [13] and X = H taken from [14]. For series *VIII*, X = 4-N(CH$_3$)$_2$, 4-OCH$_3$, 4-CH$_3$, H, 4-F, 3-OCH$_3$, 4-Cl, 4-CN, 4-NO$_2$, 3-NO$_2$, 3-Cl, 4-Br, 3-F, 4-CH(CH$_3$)$_2$, 4-OH, 4-N(C$_2$H$_5$)$_2$, 3-OH, 3-CH$_3$, 3-Br taken from [15], X = 3,4-O$_2$CH$_2$ taken from [16], X = 3-aza, 4-aza taken from [17], X = 3,4-Cl$_2$ taken from [14] and X = 4-C$_6$H$_5$ taken from [18].

In the case of diphenylketones *IX* the results of $v(C=O)$ *vs.* σ correlation were taken from [19].

Results and discussion

As it was shown in our earlier paper [6] the difference between $C=O$ stretching vibrational frequency of substituted and unsubstituted carbonyl compounds $v(C==O)_k - v(C=O)_0$ can be described by the following simple equation

$$v(CO)_k - v(CO)_0 \sim \sqrt{\varkappa(CO)_k} - \sqrt{\varkappa(CO)_0} \approx k\pi_{CO,k}\Delta\alpha_k \qquad (1)$$

where the $\varkappa(CO)_k$ and $\varkappa(CO)_0$ represent the $C=O$ bond force constant of

a substituted and unsubstituted compound, respectively and $\pi_{CO,k}$ stands for the so-called bond-atom polarizability [20]. The validity of this equation is conditioned by the existence of the relation between the carbonyl stretching frequency $v(CO)$ and bond order $p(CO)$ (eqn (2)) [21] verified by a number of authors [22—25].

$$v(CO) = kp(CO) + q \qquad (2)$$

Since the proportionality constant k in both eqns (1) and (2) is the same we may suppose that eqn (1) will be valid irrespective of the type of structural skeleton of the parent carbonyl compound, at least for derivatives satisfying eqn (2). Eqn (1) resembles the Hammett type correlation between the carbonyl stretching frequencies (expressed alternatively in terms of wavenumbers $\tilde{v}$) and the substituent constants σ (eqn (3))

$$\tilde{v}(CO)_k = \tilde{v}(CO)_0 + \varrho\sigma \qquad (3)$$

Combining eqns (3) and (1) one can expect the correlation between the experimental ϱ constants and theoretical bond-atom polarizabilities in a series of structurally related compounds. The validity of such a correlation was verified in our recent paper [6] on a rather extensive experimental material.

In the present paper our aim was to investigate the differences in the substituent effect transmission between s-*cis* and s-*trans* conformations of α,β-unsaturated carbonyl compounds. Since the corresponding subtle variations are crucially connected with the electron repulsion the simple HMO perturbation theory cannot be used for such study. For that reason we have used recently proposed SCF-LCI perturbation theory [3, 5]. Since in the framework of this theory the polarizabilities cannot be expressed analytically, we have approximated them numerically according to the equation

$$\pi_{CO,k} = \frac{\partial p(CO)}{\partial \Delta\alpha_k} \approx \frac{p(CO)_k - p(CO)_0}{\Delta\alpha_k} \qquad (4)$$

In this equation $p(CO)_0$ represents the $C = O$ bond order in unsubstituted parent compound and $p(CO)_k$ the bond order in the same compound perturbed ("substituted") in position k by the perturbation $\Delta\alpha_k$. In our case we have used the perturbation $\Delta\alpha_k = -1$ eV. Calculations were performed by the standard SCF method in π approximation complemented by subroutine performing the SCF-LCI perturbation corrections.

Following parameters were used for calculations: $\beta_{CC} = 2.318$ eV, $\beta_{CO} = \beta_{CC}$, $IP_C = 11.42$ eV, $IP_O = 17.7$ eV, $\gamma_{CC} = 10.84$ eV, $\gamma_{OO} = 15.23$ eV. Gamma integrals were approximated according to *Mataga* and *Nishimoto* [26]. Idealized planar geometry was accepted for all compounds with bond lengths $r_{CC} = 0.140$ nm, $r_{CO} = 0.125$ nm and idealized valence angles 120°.

Calculated polarizabilities together with the corresponding experimental ϱ constants for series *I—IX* are summarized in Table 1.

Table 1

Statistical results of $\bar{\nu}(CO)$ *vs.* σ correlations and SCF bond-atom polarizabilities for series of compounds *I—IX*

| Series	ϱ^a/cm^{-1}	r^b	n^c	s^d/cm^{-1}	$\pi_{CO,\kappa}^e/eV^{-1}$
I	$10.79 + 0.88$	0.968	12	1.2	-0.0015
II	$8.22 + 0.89$	0.946	12	1.2	-0.0016
III	$9.06 + 0.72$	0.967	13	0.8	-0.0014
IV	$7.50 + 1.09$	0.901	13	1.2	-0.0011
Va	$8.83 + 0.56$	0.988	8	0.5	-0.0018
VI	$1.53 + 0.47$	0.801	8	0.4	$-0.0032^f, -0.0014^g$
VII	$9.94 + 0.82$	0.968	12	1.2	-0.0014
VIII	$17.17 + 1.14$	0.955	24	2.6	-0.0025
IX	$11.87 + 1.24^h$	0.913^h	20^h	2.0^h	-0.0025

a) Slope of $\bar{\nu}(CO)$ *vs.* σ correlation; b) correlation coefficient; c) number of compounds used in correlation; d) standard deviation; e) bond-atom polarizability relating to the $C=O$ bond and carbon atom in *para* position of the substituted benzene ring; f) calculated for s-*cis* conformation; g) calculated for s-*trans* conformation; h) values taken from [19].

Since, as demonstrate the experimental data, the substituent effect transmission in α,β-unsaturated carbonyl derivatives is considerably influenced by the molecular conformation, we need to know for our calculations the actual structure of the investigated compounds. For a majority of studied series (*I—IV* and *VII*) both the configuration and the conformation have been assigned by spectral methods [8—10, 13, 27—30]. For substituted benzaldehydes *VII* a planar conformation has been proved by investigation of dipole moments and molar Kerr constants [31]. For the remaining compounds *V* and *VI* synthesized by *Duke* and *Boykin* [11] only the configuration but not the conformation was known. We have tried therefore to assign the carbonyl stretching frequencies of (*E*)-1,2-diphenyl-3-(X-phenyl)propenones (*V*) (employed in the present study) to the one of the two possible planar conformations s-*cis* (*Va*) and s-*trans* (*Vb*) using comparison with available model compounds.

Comparing ethyl (*E*)-s-*cis*-cinnamates (*X*) with ethyl (*E*)-s-*cis*-α-cyanocinnamates (*XI*) (Ref. [32]) we can ascertain that the substitution by the electron-withdrawing cyano group in the position α causes a significant increase of carbonyl
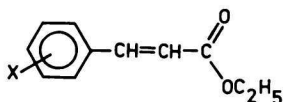

X
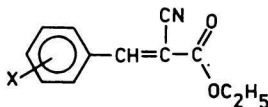
XI

stretching frequency ($\Delta\tilde{v}(C=O) = 14.5$—$18.0$ cm^{-1}). Comparing analogically the $\tilde{v}(C=O)$ values of (*E*)-1,2-diphenyl-3-(X-phenyl)propenones (*V*) [11] with those of one of the conformations of (*E*)-1-phenyl-3-(X-phenyl)propenones (*I* or *II*) [8] we can expect a similar frequency increase due to the electron-withdrawing effect of the phenyl group in α position. The comparison with s-*cis* conformation *II* renders a quite opposite result; the $\tilde{v}(C=O)$ values of compounds *V* are lower ($\Delta\tilde{v}(C=O) = 11.2$—$13.5$ cm^{-1}), which is in disaccordance with the significant $-I$ effect of the phenyl group. The carbonyl stretching frequencies of compounds *V* are, however, in harmony with those of s-*trans* conformation of (*E*)-1-phenyl-3-(X-phenyl)propenones (*I*); the wavenumber increase caused by the phenyl group being $\Delta\tilde{v}(C=O) = 6.5$—$9.7$ cm^{-1}. The comparison of inductive Taft substituent constants, $\sigma^*(C_6H_5) = 0.66$ with $\sigma^*(CN) = 3.55$ taken from [33] explains reasonably the difference in the $\Delta\tilde{v}(C=O)$ values caused by substitution of α,β-unsaturated ketones in the position α by phenyl and cyano group, respectively.

It follows from the above discussion that (*E*)-1,2-diphenyl-3-(X-phenyl)-propenones (*V*) exist prevailingly in s-*trans* conformation (*Va*), which is probably

Va   *Vb*
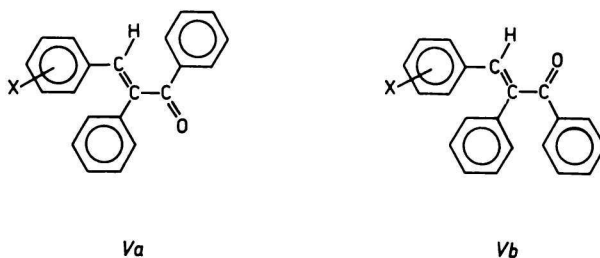
sterically more advantageous comparing to the s-*cis* conformation (*Vb*). It was demonstrated also in other cases [34, 35] that α-substituted α,β-unsaturated carbonyl compounds exist exclusively in s-*trans* conformation, whereby the corresponding unsubstituted parent compounds usually exhibit an equilibrium mixture of both s-*trans* and s-*cis* conformers.

Now having assigned the structure of investigated compounds we can interpret the ϱ constants of $v(C=O)$ *vs.* σ correlations using theoretical approximate values of bond-atom polarizabilities $\pi_{CO,k}$. Fig. 1 documents a satisfactory agreement between the theory and experiment. In harmony with the expectation the regression line passes through the origin. Some points nevertheless deviate from the line and we have to discuss the origin of these deviations. Besides other factors, probably the most important requirement for the existence of ϱ *vs.* $\pi_{CO,k}$ correlation is the planarity of the whole conjugated skeleton. This may be the reason that because of nonplanar structure of diphenylketones *IX* [36] the corresponding theoretical quantity (calculated for an idealized planar structure)
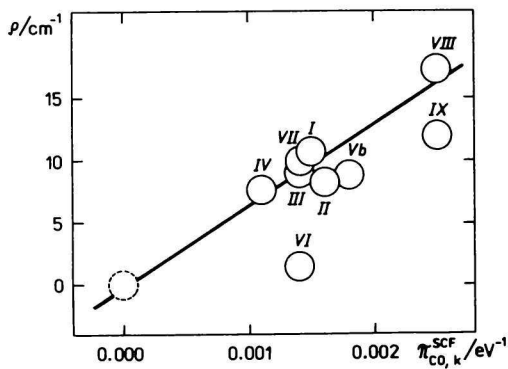
Fig. 1. Plot of experimental ϱ constants of $\bar{v}(CO)$ vs. correlations against SCF bond-atom polarizabilities for series of compounds I—IX.

does not fit the regression line. The same is true in the case of (Z)-1,2-diphenyl-3-(X-phenyl)propenones (VI) in which the steric interactions cause significant deviations from coplanarity between carbonyl group and substituted benzene ring [11]. On the other hand, (E)-s-trans-1,2-diphenyl-3-(X--phenyl)propenones (Vb) fit the regression line in Fig. 1 satisfactorily, which is in a good agreement with experimental evidences on their nearly planar structure.

The above results demonstrate that the proposed simple theoretical approach is able not only to predict the ϱ constants of the $v(C=O)$ vs. σ correlations with a reasonable accuracy, but also it can be used to assign the preferred configuration and conformation of α,β-unsaturated carbonyl compounds.

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