

Determination and structural correlation of pK_a values of *p*-substituted *trans*- β -aroylacrylic acids

Lidija Pfendt^a, Gordana Popović^b, Milka Kostić^c, Ljubomir Stevović^c, Branko Drakulić^c and Ivan Juranić^{a,*}

^aFaculty of Chemistry, University of Belgrade, PO Box 158, 11000 Belgrade, Yugoslavia

^bFaculty of Pharmacy, University of Belgrade, PO Box 146, 11000 Belgrade, Yugoslavia

^cCenter for Chemistry, IChTM Belgrade, 11000 Belgrade, Yugoslavia

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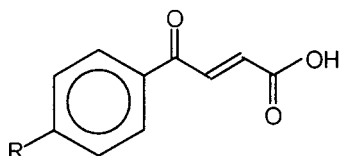
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For a series of 10 *p*-substituted *trans*- β -aroylacrylic acids, pK_a values were determined spectrophotometrically in water at 25°C and at ionic strength 0.1 M (NaCl). The thermodynamic pK_a values were correlated with Hammett σ_p constants.

Aroylacrylic acid derivatives are convenient substrates for the evaluation of structure reactivity relationships^{5,6} due to the presence of the system of conjugated double bonds, between the benzene ring and the carboxyl group. Further interest in investigating these acids arises from their biological activity.^{7–10}

The general formula of the *p*-substituted *trans*- β -aroylacrylic acids (AAA) studied in this work is given in Scheme 1.



R = H, Me, Et, Prⁱ, Bu^t, OH, OMe, F, Cl and Br

Scheme 1

The acidity constants for these acids were determined spectrophotometrically¹⁷ in an aqueous medium at 25°C and at an ionic strength of 0.1 M (NaCl). A survey of the stoichiometric (pK_a^c) and thermodynamic (pK_a) constants obtained is presented in Table 2, together with Hammett σ_p and σ_p^+ substituent constants.

A correlation was established between the pK_a values obtained and Hammett substituent constants. The corresponding Hammett equation ($pK_a = pK_a^0 - \rho\sigma_p$)²¹ obtained in this case is:

$$pK_a = 3.32 - 0.60\sigma_p \quad (2)$$

with regression parameters $r = 0.988$, $s = 0.02$ and $n = 10$.

Figure 3.

The LFER analysis enabled the elucidation of the mechanism of the transmission of the polar effect through the aromatic ring and the conjugated side chain. As expected, when correlation of equilibrium constants of protolytic reactions is concerned, the ρ value is positive, meaning that the extent of acid dissociation is increased by electron-withdrawing substituents. For the *trans*- β -aroylacrylic acid series $\rho = 0.60$, showing that this reaction series is less sensitive to polar influences of substituents than the dissociation of benzoic acid under the same conditions²² ($\rho = 1.00$). This result is not surprising since the reaction site is partially protected from the effect of the substituent on the aromatic nucleus by insertion of the CO–CH = CH group.

Since the structure of *trans*- β -aroylacrylic acids does not permit resonance between the substituent and the carboxyl group, the extent of resonance contribution to the overall sub-

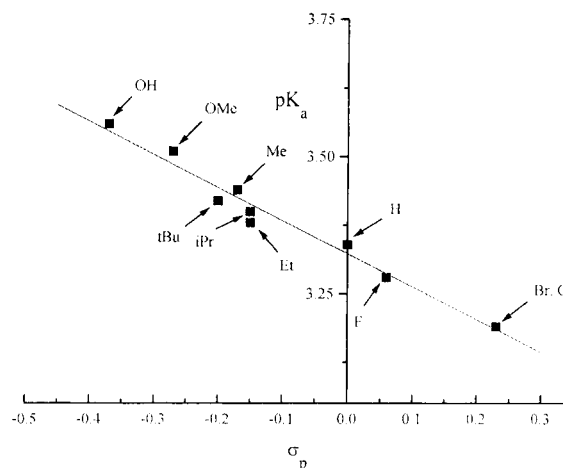


Fig. 3 Plot of pK_a values of *trans*- β -aroylacrylic acids against the corresponding Hammett σ_p constants.

stituent polar effect was checked using Yukawa–Tsuno equation.²³ In this way, the correlation is slightly improved and the weighting of σ_p^+ was only 13%, indicating a small resonance contribution to the polar effect of the *p*-substituent to the carboxylic group and/or its anion.

Results of MNDO-PM3 calculations reveal that despite the double bonds' conjugation, there is a torsional distortion between the aromatic ring and the side-chain. This torsional deformation is similar in the anion and in the neutral molecule. The major deformation in the anion is the out-of-plane rotation of the $-\text{CO}_2^-$ group, causing the carboxylate group to assume a nearly perpendicular position to the rest of the molecule. This could be the basis for an understanding of the hypsochromic effect in the anion. The obviously reduced delocalization in the anion is related to a larger HOMO–LUMO gap, and, consequently, to the larger excitation energies.

Techniques used: UV-visible spectrophotometry, semiempirical MO calculations (MNDO-PM3)

References: 24

Table 1: Spectral characteristics of *trans*- β -aroylacrylic acids.

Table 3: Torsional angles of the aromatic ring in *trans*- β -aroylacrylic acids for various substituents, calculated by MNDO-PM3 method.

Fig. 1: Absorption spectra of AAA and its *p*-chloro and *p*-hydroxy derivatives, at variable pH.

Fig. 2: Plots for determination of pK_a^c of AAA and its *p*-chloro and *p*-hydroxy derivatives.

* To receive any correspondence. E-mail: ijuranic@chem.bg.ac.yu

Table 2 Survey of the determined pK_a^c and pK_a values of *trans*- β -aroylacrylic acids, and Hammett σ_p and σ_p^+ constants

R	H	Me	Et	Pr ⁱ	Bu ^t	OH	OMe	F	Cl	Br
pK_a^c	3.12 ± 0.04	3.22 ± 0.02	3.16 ± 0.02	3.18 ± 0.02	3.20 ± 0.03	3.34 ± 0.03	3.29 ± 0.04	3.06 ± 0.03	2.97 ± 0.02	2.97 ± 0.02
pK_a	3.34	3.44	3.38	3.40	3.42	3.56	3.51	3.28	3.19	3.19
σ_p	0.00	-0.17	-0.15	-0.15	-0.20	-0.37	-0.27	0.06	0.23	0.23
σ_p^+	0.00	-0.31	-0.30	-0.28	-0.26	-0.92	-0.78	-0.07	0.11	0.15

Fig. 4: Geometries of AAA and its anion calculated by MNDO-PM3 method.

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