

Molecular Orbital Aspects of Substituent Effects

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The charge densities at the exocyclic reaction centers of para-substituted benzoic acids calculated by the INDO-MO method correlate with the Hammett σ_p constants.

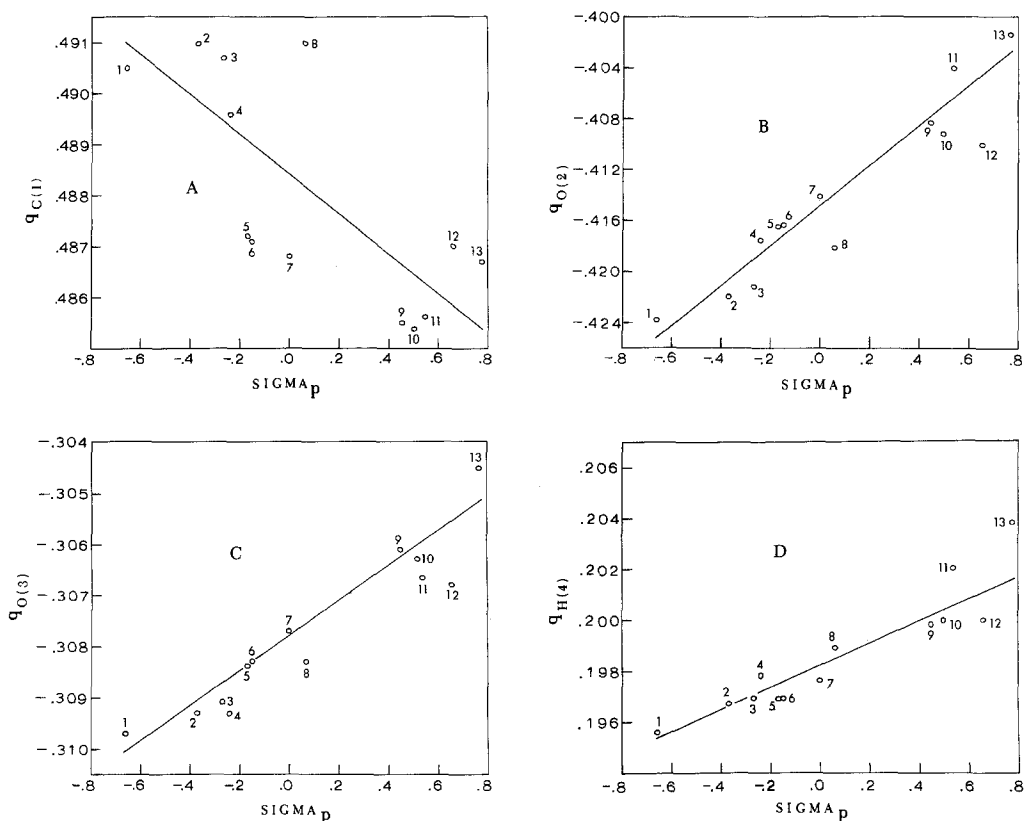


Fig. 1 A-D. Para-substituted benzoic acids. Correlations between charge densities and σ_p . A for carbonyl carbon, B for carbonyl oxygen, C for hydroxyl oxygen, D for carboxylic acid hydrogen (I). Numbers indicate: 1 = NH_2 , 2 = OH , 3 = OCH_3 , 4 = OC_2H_5 , 5 = CH_3 , 6 = C_2H_5 , 7 = H , 8 = F , 9 = COOH , 10 = COCH_3 , 11 = CF_3 , 12 = CN , 13 = NO_2

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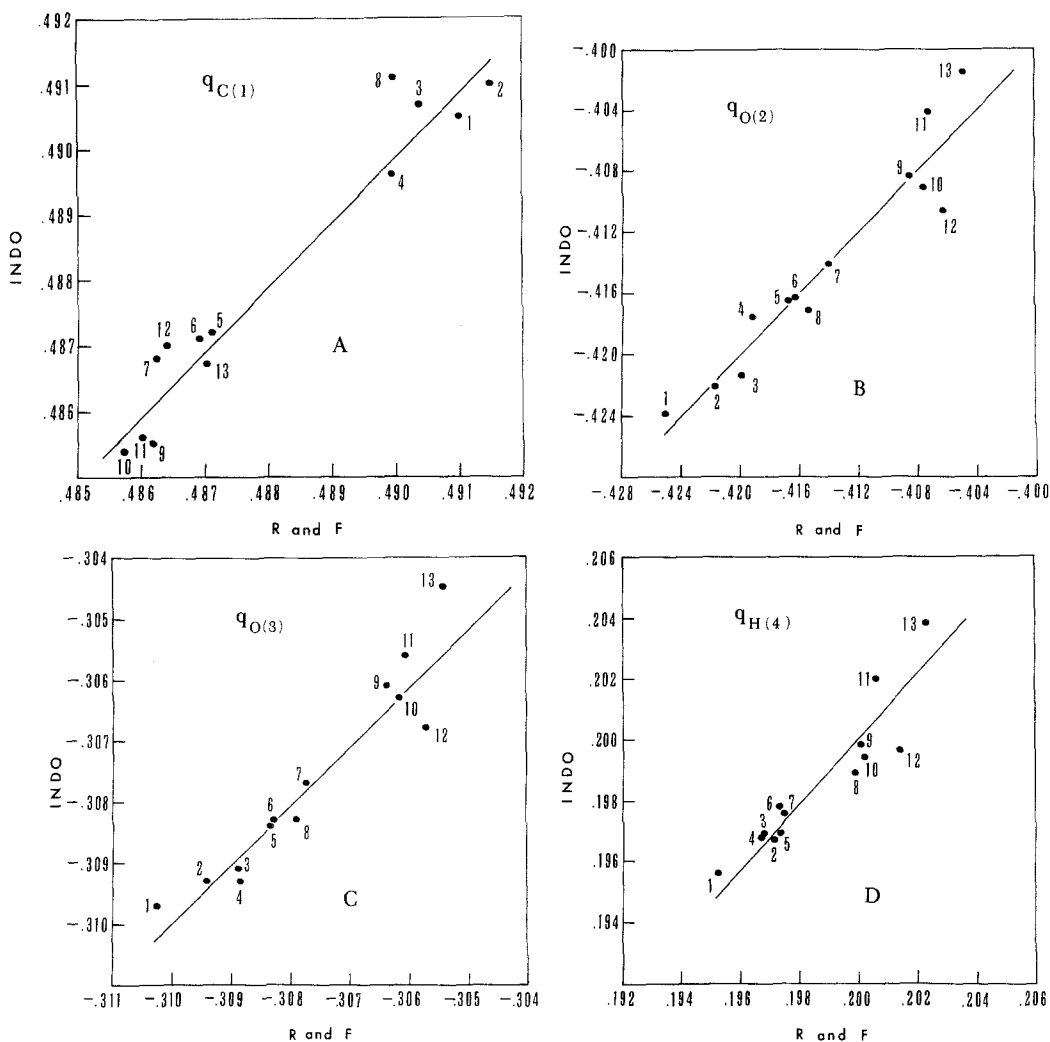
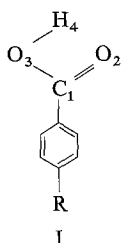


Fig. 2 A–D. Para-substituted benzoic acids. INDO charge densities versus charge densities obtained from resonance and field constants. A for carbonyl carbon, B = carbonyl oxygen, C = hydroxy oxygen, D = carboxylic acid hydrogen. Numbers indicate: 1 = NH₂, 2 = OH, 3 = OCH₃, 4 = OC₂H₅, 5 = CH₃, 6 = C₂H₅, 7 = H, 8 = F, 9 = COOH, 10 = COCH₃, 11 = CF₃, 12 = CN, 13 = NO₂. For the calculations of charge densities from resonance (*R*) and field (*F*) constants, the following regression equations were used: (A) $q_{C_1} = 0.4862 + 0.0086(-0.80R + 0.20F)$, (B) $q_{O_2} = -0.4140 + 0.0224(0.74R + 0.26F)$, (C) $q_{O_3} = -0.3077 + 0.00534(0.71R + 0.29F)$, (D) $q_{H_4} = 0.1975 + 0.0074(0.47R + 0.53F)$

Although empirical relationships between substituents and chemical reactivities are well established [1, 2], the origin of the substituent effects and the applications of these relationships to more complicated molecules such as randomly poly-substituted polycyclic aromatic compounds are not straightforward. Aiming at explaining the electronic nature of the reaction centers effected by the substituents, we report herein correlations between the Hammett σ_p constants [1, 2] and total atomic charge densities at the exocyclic reaction centers in 13 para-substituted

benzoic acids (I) (Figs. 1 and 2).



The electronic structures of these compounds were calculated by the self-consistent field molecular orbital method on the INDO (Intermediate Neglect of Differential Overlap) level of approximation [3], which is known to produce the best values of charge densities, dipole moments and spin densities among the semi-rigorous SCF-MO schemes [4]. Similar quantum mechanical approach to the substituent effects has been made by Brownlee and Taft [5] who found a good correlation between σ_R^0 and total π charge densities of the ring carbon atoms in mono-substituted benzene by the CNDO/2 method [6]. Although the substituents effect the delocalized π electrons and orbital energies of the aromatic ring, we focused our interest on the localized exocyclic reaction centers. Benzoic acids were chosen for the model study, because the original Hammett σ scale has been taken from the ratio of the dissociation constants of the substituted benzoic acids to the unsubstituted one, and because the carbonyl carbon and carbonyl oxygen are the reaction centers where the attack of the hydroxy anion or proton ligand is rate determining step in the base catalyzed hydrolysis or acid catalyzed esterification of benzoic acids.

Fig. 1 shows a good correlation between calculated charge densities and σ_p constants. The calculated charge densities were further separated into two independent electric effects; resonance (*R*) and field (*F*) effects [7] (Fig. 2). The results show that the contribution of the resonance effect on the charge densities of the exocyclic reaction centers calculated by the INDO method is greater (80% *R* for q_{C_1} , 74% *R* for q_{O_2} , 71% *R* for q_{O_3} and 47% *R* for q_{H_4}) than that obtained by statistically averaged experimental values (53% *R*) [7]. It has been shown also that the resonance contribution varies from one position to the other.

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