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Infrared and Raman Studies of Carbonyl Group Frequencies of *p*-Substituted Benzoic Acids in the Crystalline State

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Infrared and Raman carbonyl stretching frequencies for *p*-substituted benzoic acids in the crystalline state were measured and discussed in terms of the Hammett equation and hydrogen bond strength.

INTRODUCTION

It was found¹ that $R_{O...O}$ distances in cyclic dimers of *p*-substituted benzoic acids in the crystalline state do not follow the Hammett rule. The $R_{O...O}$ values often serve as an approximate measure of hydrogen bond strength.² Since substituent constants σ_p and $R_{O...O}$ express the Brönsted and the Lewis acidity of the carboxylic group in solution and in the crystalline state, respectively, a linear dependence between them was expected. Lack of this dependence was explained¹ in terms of packing forces, which are supposed to affect the $R_{O...O}$ distance much more strongly than may be expected from the substituent effect. Since two molecules of carboxylic acid form a centrosymmetric dimer this leads to coupling of COOH oscillators. In consequence, symmetric and antisymmetric modes are observed in Raman and IR spectra, respectively. Analysis of a vast amount of IR and Raman spectral data as well as the geometry of the H-bond has led Novak² to the conclusion that spectral characteristics of the carbonyl group vary in a regular way with $R_{O...O}$ distances of the H-bond — at least for a broad meaning of mutual correlation.

The purpose of this paper is to compare the substituent effect on carbonyl group frequencies ν_{CO} in *p*-substituted benzoic acids in the crystalline state and in solution as well as to discuss the observed differences in the substituent effect on the geometry of the H-bond. Therefore IR and Raman carbonyl group frequencies were measured in the crystalline state for 10 *p*-substituted benzoic acids for which accurate X-ray diffraction structural data are available.

RESULTS AND DISCUSSION

Table I presents ν_{CO} -values measured for 10 para substituted benzoic acids in the crystalline state by the use of IR and Raman techniques compared with IR data for dimers measured in CCl_4 solutions³ and $R_{O...O}$ distances for the H-bridge from X-ray diffraction studies. When ν_{CO}^{IR} and ν_{CO}^R are plotted against σ_p we obtain

$$\nu_{CO}^{IR} = 15.3 \sigma_p + 1689.2 \quad (1)$$

with $r = 0.910$, and

$$\nu_{\text{CO}}^{\text{R}} = 11.9 \sigma_p + 1627.6 \quad (2)$$

TABLE I

IR and Raman Carbonyl Stretching Vibration Bands in Dimers of Para Substituted Benzoic Acids Compared with $R_{\text{O}\dots\text{O}}$ Distances and $\nu_{\text{CO}}^{\text{IR}}$ Measured in Solution³

X-PH-COOH X =	$\nu_{\text{CO}}^{\text{IR}}$ (cm^{-1})	$\nu_{\text{CO}}^{\text{Raman}}$ (cm^{-1})	$\nu_{\text{CO}}^{\text{IR}*}$ (solution) ³ (cm^{-1})	$R_{\text{O}\dots\text{O}}$ (\AA)
		1638		
1. NO ₂	1701	1630	1706.1	2.622(7) ⁶
2. CN	1699	1634	1704.9	2.610(6) ⁷
3. Cl	1690	1626	1697.1	2.618(2) ⁸
4. Br	1639	1631	—	2.646(4) ⁹
5. F	1694	1628	1698.3	2.618(2) ¹⁰
6. H	1698	1634	1695.9	2.627(1) ⁵
7. CH ₃	1685	1625	1695.7	2.630(5) ¹¹
8. OCH ₃	1684	1623	1689.9	2.632(2) ¹²
9. OH	1683	1625	1691.6	2.658(2) ¹³
	1678			2.642(3) ¹⁴
10. NH ₂ (A)		1618	1685.2	2.610(5) ¹⁴
(B)	1627			
11. 2,4-diNO ₂	1722	1666	—	2.656(3) ¹⁵

* Frequencies measured for dimers of *p*-substituted benzoic acids in CCl₄ solutions.

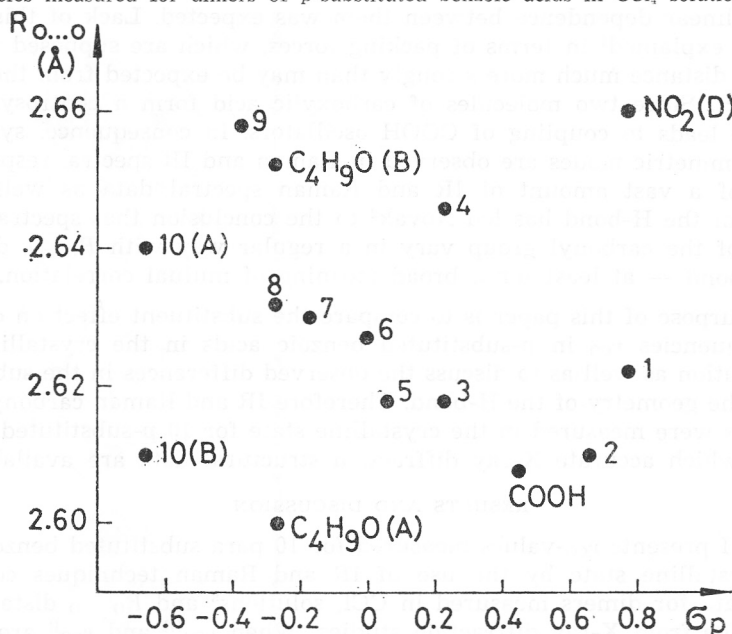


Figure 1. Dependence of $R_{\text{O}\dots\text{O}}$ distances in dimers of *p*-substituted benzoic acids in crystalline state on substituent constants σ_p . Assignments as in Table I except additional points which are denoted by chemical symbols. References for C₄H₉O,¹⁶ COOH¹⁷ and NO₂(D)¹⁸.

with $r = 0.883$. These plots are considerably more acceptable than that between $R_{O...O}$ and σ_p presented in Figure 1, nevertheless they express only a rough tendency of mutual dependence. In contrast, while plotting ν_{CO}^{IR} measured in CCl_4^3 against σ_p for the same group of benzoic acids, the resulting regression was obtained

$$\nu_{CO}^{IR} (CCl_4) = 13.9 \sigma_p + 1695.7 \quad (3)$$

with $r = 0.973$.

It may be concluded at this moment that the force field describing ν_{CO} vibration in dimers of *p*-substituted benzoic acids in the crystalline state is much less affected by packing forces than is the geometry of the H-bridge.

Another problem worth mentioning is the complex shape of the ν_{CO} -band which in the case of *p*-NH₂-Ph-COOH leads to two maxima (cf. Table I) in the CO-stretching region. In this particular case this effects can be explained by the existence of two chemically different dimers (denoted A and B in Table I) in the asymmetric unit of the crystal lattice. They have different geometries, as displayed by values of $R_{O...O}$ in Table I. However the broad shape of the CO-vibration band also exists in other cases and needs explanation.

An attempt at an explanation of this problem may-be based on the thorough studies by Hayashi and Umemura⁴ who found a weak band at 1710 cm^{-1} and strong one at 1688 cm^{-1} in IR spectra of crystalline benzoic acid at

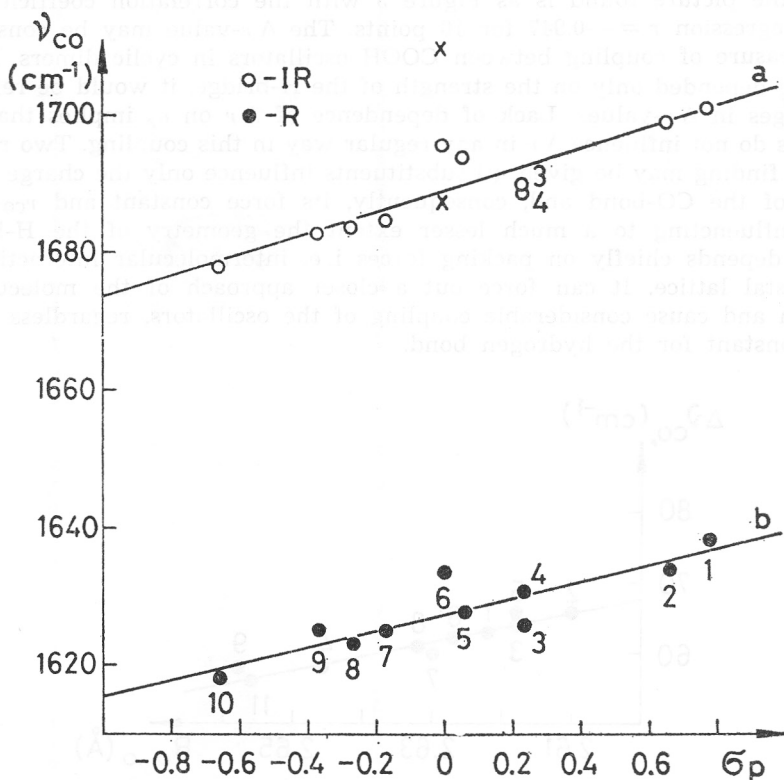


Figure 2. Dependences of ν_{CO} -values in IR (a) and Raman (b) spectra of dimers of *p*-substituted benzoic acids in crystalline state on substituent constant σ_p . Assignments as in Table I. Crosses for benzoic acid cf. text.

293 K. The authors revealed a regularity: with a temperature decrease the band at 1710 cm^{-1} tends to increase, while the one at 1668 cm^{-1} disappears. Finally, at about 7 K only one band at 1710^{-1} is observed. Both frequencies have been assigned to the C=O stretching vibrations of lower energy (A) and higher energy (B) configurations, respectively. Recent crystal structure data for benzoic acid obtained by Feld et al.⁵ with X-rays at room temperature and supported by a neutron-diffraction study at temperatures down to 5 K seem to confirm these conclusions. It has been stated that both configurations coexist in the crystal but only at room temperature. At 5 K the crystal consists of the A-configuration and the acidic H-atom is bonded to the oxygen of the C—O bond. In Figure 2a the Hayashi and Umemura⁴ data for benzoic acid are represented by crosses. It is immediately apparent that their ν_{CO} at 1688 cm^{-1} i. e. for the room temperature stable configuration of benzoic acid obeys the Hammett line much better than our data point which reflect the superposition of both bands reported by Hayashi and Umemura.⁴ Nevertheless, the Raman spectra of benzoic acid show the single band at 1634 cm^{-1} .

Finally we attempted to relate $\nu_{\text{CO}}^{\text{R}}$ and $\nu_{\text{CO}}^{\text{IR}}$ with H-bond strength measured approximately by $R_{\text{O}\dots\text{O}}$ -values. Unfortunately, the results obtained were discouraging; the correlations found were insignificant with r about 0.6. However, if the difference $\Delta\nu_{\text{CO}} = \nu_{\text{CO}}^{\text{IR}} - \nu_{\text{CO}}^{\text{R}}$ is defined and plotted against $R_{\text{O}\dots\text{O}}$ the picture found is as Figure 3 with the correlation coefficient for linear regression $r = -0.947$ for 10 points. The $\Delta\nu$ -value may be considered as a measure of coupling between COOH oscillators in cyclic dimers. If this coupling depended only on the strength of the H-bridge, it would be reflected in changes in $\Delta\nu$ -values. Lack of dependence of $\Delta\nu$ on σ_p implies that substituents do not influence $\Delta\nu$ in any regular way in this coupling. Two reasons for this finding may be given: (i) substituents influence only the charge distribution of the CO-bond and, consequently, its force constant and ν_{CO} -value, while influencing to a much lesser extent the geometry of the H-bridge, (ii) $\Delta\nu$ depends chiefly on packing forces i. e. intermolecular interactions in the crystal lattice. It can force out a closer approach of the molecules in question and cause considerable coupling of the oscillators, regardless of the force constant for the hydrogen bond.

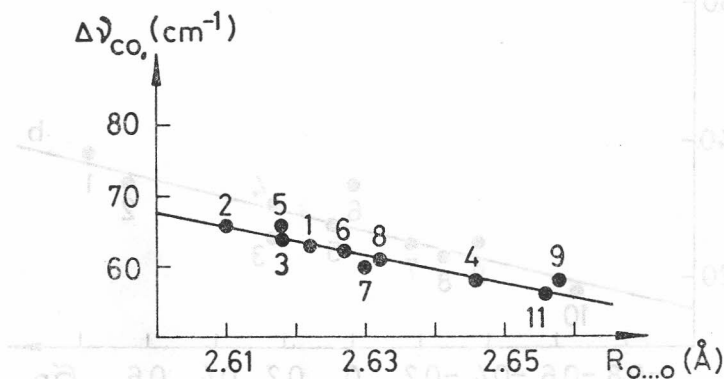


Figure 3. Plot of $\Delta\nu_{\text{CO}} = \nu_{\text{CO}}^{\text{IR}} - \nu_{\text{CO}}^{\text{Raman}}$ against substituent constants σ_p . Assignments as in Table I.

Another problem concerned the adequate choice of the $R_{0\dots 0}$ value for *p*-nitrobenzoic acid. Two refinements of crystal structure were performed^{7,20} for two different crystal modifications. Identification of our sample of *p*-nitrobenzoic acid leads to the conclusion that it is the same as that studied by Groth.⁶ Hence the Groth $R_{0\dots 0}$ value was used in drawing the regression in Figure 3.

EXPERIMENTAL

Gently ground samples were introduced into the powder sample holder. Raman spectra were recorded at room temperature on a Cary 82 spectrometer by Varian, supplied with an argon ion laser of Spectra Physics, type 164-03. The green line at 514.5 nm was used for excitation. The power of light in samples was 100 mwatt; the spectral band slitwidth 1-2 cm^{-1} .

The infrared spectra were recorded on a UR-20 spectrometer. All compounds were compressed into KBr pellets. Spectra were recorded in a range of 1500-1900 cm^{-1} .

X-ray analysis of *p*-nitrobenzoic acid was performed with the aid of a DRON 3 diffractometer made in the USSR. The X-ray pattern obtained from the nonoriented aggregate shows reflections corresponding to the most important reflections of *p*-nitrobenzoic acid. The 020 and 040 reflections are rather strong. With $d(020) = 2.59$ Å and $d(040) = 1.29$ Å the *b* parameter is 5.18 Å and 5.16 Å, respectively, which agrees well with $b = 5.153$ Å characteristic for modification II of *p*-nitrobenzoic acid described by Groth.⁶

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SAŽETAK

Frekvencije karbonilne grupe u infracrvenim i Raman spektrima za *p*-supstituirane benzojeve kiseline u kristalnom stanju

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Izmjerene su frekvencije istezanja karbonilne grupe u infracrvenim i Raman spektrima za *p*-supstituirane benzojeve kiseline u kristalnom stanju i razmatrane u okvirima Hammettove jednadžbe i jakosti vodikove veze.

Elucidation of the Structure of Some Potential Antidiabetic Pyrazolin-5-ones Using Polarographic Technique

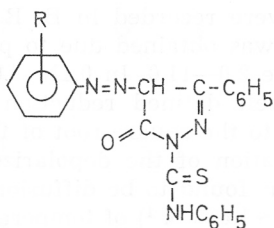
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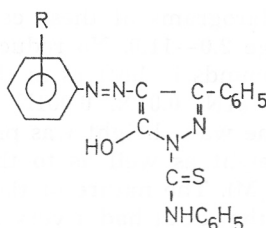
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The polarographic reduction behaviour of 4-arylhydrazono-*N*-arylthiocarbamoyl-3-phenyl-2-pyrazolin-5-one has been investigated to find out the existing tautomeric form. The polarographic behaviour suggests the presence of the hydrazo form. The effect of various substituents on reduction was studied and a quantitative relationship established between $E_{1/2}$ and Hammett substituent constants. The values of *m*- and *p*-derivatives fitted in a straight line from which the value of the specific reaction constant (ρ) was determined as 0.13 V. The positive value of the specific reaction constant (ρ) indicates a nucleophilic mechanism of the electrode process.

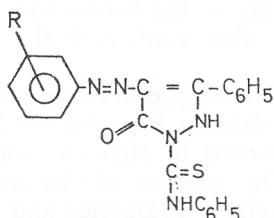
A number of pyrazolines¹⁻³ have been reported in the literature as possessing considerable antidiabetic activity. Recently some 4-arylhydrazono-*N*-arylthiocarbamoyl-3-phenyl-2-pyrazolin-5-ones have been synthesized as potential antidiabetic compounds. These compounds can exist in the following four tautomeric forms:



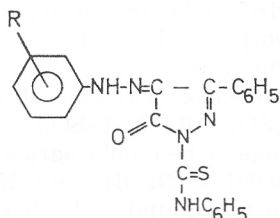
(A)



(B)



(C)



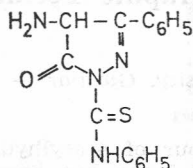
(D)

Where, R, represents various substituents.

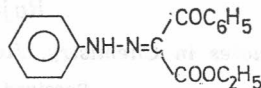
Keeping their biological importance in view a study was needed to establish the correct structure. In the present investigation the polarographic reduction behaviour of these compounds has been used to identify the existing tautomeric form. The quantitative effect of substituents has been interpreted in terms of the Hammett equation.

EXPERIMENTAL

Various compounds (I—X) listed in Table — I were synthesised by the method reported from this laboratory⁴ and their purity was checked. Two more compounds (E) and (F) were synthesized by the condensation of a suitable β -diketone with phenylthiosemicarbazide and by the condensation of a suitable β -diketone with the diazonium chloride of aniline, respectively.



(E)



(F)

Stock solution (10^{-3} M) of all these hydrazones was prepared in dimethylformamide (AnalaR). To study the effect of pH on $E_{1/2}$ B. R. Buffers⁵ were used in the pH range 2.0—11.0.

Apparatus and Procedure

The polarograms were recorded on an Elico CL-25 recording polarograph with capillary characteristic ($m^{2/3} t^{1/6}$) as $1.45 \text{ mg}^{2/3} \text{ s}^{1/2}$ at $h = 50 \text{ cm}$. The number of electrons involved in reduction was determined by the method of DeVries and Kroon⁶ using a mercury pool cathode. The temperature coefficient was determined by Nejedly's method⁷. Polarograms were recorded in 30% D.M.F. which was necessary to keep the compounds in solutions.

RESULTS AND DISCUSSION

The polarograms of these compounds were recorded in B. R. buffers in the pH range 2.0—11.0. No reduction wave was obtained due to precipitation of the compounds in buffers in the pH range 2.0—11.0. In 0.1N, 0.01N, 0.001N NaOH and 0.1N, 0.01N, 0.001N H_2SO_4 a well defined reduction wave was obtained. The wave height was proportional to the square root of the mercury reservoir height as well as to the concentration of the depolarizer (1×10^{-4} — 4.0×10^{-4} M). The nature of the waves was found to be diffusion-controlled by the fact that di/dt had a very low value ($\sim 1.6\%$ K^{-1}) of temperature coefficient along with the linear dependence of the limiting current on h . The shift of $E_{1/2}$ towards the more negative potential with increasing concentration of the depolarizer indicates the irreversible nature of the waves and the possible role of adsorption. Logarithmic analysis⁸ further confirmed the irreversible nature of the wave.

The half-wave potential shifted with varying concentrations of H_2SO_4 (0.001 N H_2SO_4 —0.1 N H_2SO_4) whereas no shift in $E_{1/2}$ was observed in the alkaline range, when polarograms were recorded in different concentrations of NaOH (0.001 N NaOH—0.1 N NaOH). The number of electrons involved in reduction was found to be four by the method of DeVries and Kroon. The values of 'n' were also determined by the method of Oldham and Perry⁹. The values of half-wave potentials together with i_d and αn are given in Table I.

TABLE I

Polarographic Characteristics of 4-Arylhydrazono-N-arylthiocarbamoyl-3-phenyl-2-pyrazolin-5-ones at 0.1 N NaOH, Conc. = 3.0×10^{-4} M

S. No.	R	$-E_{1/2}/V$	$i_d/\mu A$	$\Delta E_{1/2}/V$	an
I	H	0.96	0.750	0.00	1.10
II	2-CH ₃	0.91	0.780	0.05	1.10
III	3-CH ₃	0.98	0.750	0.02	1.20
IV	4-CH ₃	1.00	0.750	0.04	1.15
V	2-Cl	0.88	0.780	0.08	1.10
VI	3-Cl	0.96	0.735	0.00	1.15
VII	4-Cl	0.96	0.750	0.00	1.20
VIII	2-OCH ₃	0.96	0.780	0.00	1.20
IX	4-OCH ₃	1.04	0.750	0.08	1.10
X	4-OC ₂ H ₅	1.03	0.750	0.07	1.20

Out of the four possible structures proposed the first three can be excluded on the basis of the number of electrons involved in the reduction. The reduction of azo compounds¹⁰⁻¹² involves two electrons, unless¹³ a strong electron donating group such as 4-OH or 4-NH₂ is present, while hydrazo compounds reduce in a 4 electron wave. Since these compounds involve four electrons in reduction, there is only the possibility of existence of structure (D) with a hydrazo group.

In order to confirm that the hydrazono group undergoes reduction, and not the side chain —N=N— group and nuclear group —C=N— or both the nuclear groups in two 2 electron steps, the compound *N*-arylthiocarbamoyl-3-phenyl-4-amino-2-pyrazolin-5-one (*E*), which is obtained as the final product along with aniline on controlled potential electrolysis of compound (D) was synthesised. On polarographic investigation of this compound under similar experimental conditions to those of compound (D) it was observed that this compound did not give any reduction wave up to 1.6 V. This fact clearly confirms that the reduction wave obtained for compound (D) is due to the reduction of the hydrazono grouping. Further convincing evidence for the reduction of the hydrazono group in compound (D) comes from the fact that another structurally similar compound (F), which is also the precursor of the above compound, and which does not have either cyclic —N=N— or C=N groups was polarographed under similar experimental conditions. It gave only one four electron reduction wave at —0.90, V. On controlled potential electrolysis this compound (F) also gave aniline as the end product. The slightly positive potential for this compound (F) may be due to the presence of a bulky group in compound (D).

The dependence of the half-wave potential on the strength of acid indicated the participation of protons in the reduction and this fact lead to the conclusion that the fast proton transfer precedes the main electrode process. However, in the alkaline range, the $E_{1/2}$ becomes independent of the strength of NaOH i.e. proton do not take part in the pre-or rate determining step. Thus the following reduction mechanism at the electrode may be proposed in the acidic as well as in the alkaline range.

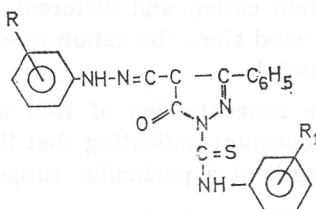


(where, R represents substituents in the phenyl ring).

whilst deviation in the case of ortho derivatives can be accounted for on the basis of steric hindrance to coplanarity. No such deviations are observed when the corrected¹⁴ values of $E_{1/2}$ for ortho derivatives are plotted against Hammett substituent constants (Figure 1b). A positive value of the specific reaction constant ($\rho = 0.13$ V) is in good agreement with reported values for hydrazones¹⁸. Moreover the substituent at the phenyl group attached to C=S i. e. CSNHC₆H₅ was also varied viz., 3-CH₃, 4-CH₃, 3-OCH₃, 4-OCH₃ and 4-OC₂H₅ in order to see the effect of substituents when they are present at a distance from the reduction site. Values of $E_{1/2}$ and i_d are given in Table II. No regular

TABLE II

Values of $E_{1/2}$ and i_d when CSNHC₆H₅ is Substituted



S. No.	R	R ₁	0.1 N NaOH	
			$-E_{1/2}/V$	$i_d/\mu A$
1.	H	H	0.95	0.750
2.	H	3-CH ₃	0.90	0.750
3.	H	4-CH ₃	0.94	0.800
4.	H	3-OCH ₃	0.90	0.800
5.	H	4-OCH ₃	0.99	0.750
6.	H	4-OC ₂ H ₅	0.92	0.750

effect was observed on reducibility, which may be due to the presence of substituents at a remote distance from the reduction site.

TABLE III

Values of Polarographic Orthoshift (Δo) for pyrazolin-5-ones in 0.1 N NaOH

R	$\Delta O/V$
Methyl	0.09
Methoxy	0.08
Chloro	0.08

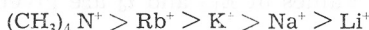
The approximate value for the non-polar contribution to the ortho effect¹⁴ is defined as the difference in $E_{1/2}$ of ortho and para substituted compounds.

$$\Delta O = (E_{1/2})_{o-x} - (E_{1/2})_p - x$$

It is evident from Table III that CH₃, OCH₃ and Cl substituents show a positive ortho shift. This indicates that the ortho derivatives are reduced at a more positive potential than their para analogues.

Effect of Cations and Anions

The effect of the size of the cation of the supporting electrolytes on the nature and shape of the wave was determined by recording the polarograms of these compounds (I—X) in the chlorides of lithium, sodium, and rubidium and in tetramethylammonium bromide. The $E_{1/2}$ shifted towards a more negative potential with increase in the size of cations. The shift in $E_{1/2}$ follows the order of increasing ionic radii.



A further check was made by recording the polarograms with supporting electrolytes having a common cation and different anions. No change in $E_{1/2}$ and i_d was observed as expected since the cation predominated in the electrical double layer at these potentials.

Furthermore, when the concentration of KCl was varied from 0.1 M to 2.5 M, $E_{1/2}$ and i_d remained constant indicating that the $E_{1/2}$ of these compounds is independent of the strength of a particular supporting electrolyte.

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SAŽETAK**Određivanje strukture nekih potencijalnih antidiabetskih pirazolin-5-ona pomoću polarografske metode***Rajeev Jain*

Ispitana je polarografska redukcija 4-arilhidrazono-*N*-ariltiokarbamoil-3-fenil-2-pirazolin-5-ona s ciljem utvrđivanja postojanja tautomernih oblika. Polarografsko ponašanje ukazuje na postojanje hidrazo forme. Ispitan je utjecaj različitih supstituenata i kvantitativno određena relacija između polovalnog potencijala i Hammett-ove supstitucione konstante. Vrijednosti za *m*- i *p*-derivate nalaze se na pravcu i iz njih je izračunata specifična konstanta reakcije (ρ) s vrijednošću od 0,13 V. Pozitivni predznak ove konstante ukazuje na nukleofilni mehanizam elektrodne reakcije.