TRANSMISSION OF INFLUENCE OF SUBSTITUENT IN 2-ARYLPYRROLE-5-CARBOXYLIC ACIDS

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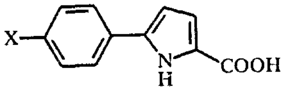
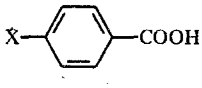
Research on the influence of substituents on the reaction centers of molecules, through various bridge groups, is still an urgent task in theoretical organic chemistry. This problem is usually solved using the Hammett equation $f = \rho\sigma + a$*, by comparing the coefficient* ρ *of the particular series of compounds under investigation with the coefficient* ρ_0 *of a reference series of compounds. The ratio of coefficients* $\rho/\rho_0 = \pi'$*, which is called the transmission factor, characterizes structural changes of the bridge group [1, 2].*

In the work reported here we undertook a quantitative evaluation of the conduction of electronic effects of substituents through a pyrrole ring, using methods of IR spectroscopy and quantum chemistry.

To this end, we investigated the IR spectra of 2-arylpyrrole-5-carboxylic acids



with a subsequent comparison of the frequencies of stretching vibrations of the C═O groups with ν C═O of the benzoic acid series



The spectra of solid samples of the 2-arylpyrrole-5-carboxylic acids (in tablets with KBr0 have a form that is characteristic for dimers of carboxylic acids. There are two broad bands in the 2400-2800 and 2800-3000 intervals and an intense band at 1660 cm^{-1} pertaining to vibrations of bound OH and CO groups. Spectra of solutions of these compounds in CCl_4 contain, along with the bands of associates, two bands at 3450 and 1710 cm^{-1} that increase in intensity with decreasing concentration; these bands pertain to vibrations of OH and CO monomers (Table 1). The difference in νC═O frequencies for the monomers (in CCl_4) and for the dimers (solid substances) is practically constant, ~50 cm^{-1}. It can be seen from Table 1 that the frequencies of stretching vibrations of free and bound C═O groups are sensitive to the influence of the para-substituent, which is separated by two rings. The C═O frequency decreases with increasing donor properties of X in the series Cl > H > Alk > OMe, with a simultaneous increase of νOH. An analogous relationship is observed in para-substituted benzoic acids [3].

In order to establish a quantitative relationship between νC═O and the natured of the substituent, we carried out a correlation analysis of experimental data in the series of 2-arylpyrrole-5-carboxylic acids (I) and benzoic acids (II), and also

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TABLE 1. Frequencies (ν, cm^{-1}) of Stretching Vibrations of CO and OH Groups in 2-Arylpyrrole-5-carboxylic Acids

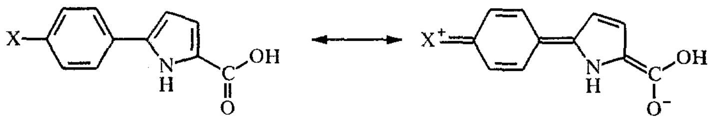
X	C=O of dimer	C=O of monomer	OH of monomer
H	1664	1716	3536
Me	1662	1714	3540
Et	1661	1714	3540
Cl	1666	1718	3534
OMe	1659	1709	3542

TABLE 2. Correlation of Frequencies of Stretching Vibrations of Free C═O Group with σ^+ Constants

Series	a	ρ	r	s_0	n
I	1715±0,35	9,60±0,86	0,991	0,60	5
II	1745±0,34	9,79±0,76	0,982	0,90	7
III	1707±0,38	9,14±0,49	0,990	1,00	7
IV	1694±0,27	9,13±0,55	0,988	0,85	10
V	1731±0,34	9,17±0,54	0,993	1,00	10

in the reaction series XC_6H_4COY, where Y = H(III), Me (IV), or OMe (V) [4], with the σ_p and σ^+ constants of the substituents X. The highest coefficient of correlation was observed in all of the series when using the electrophilic constants of the substituents X (σl^+) [5]. In Table 2, for each series (I-V), we have listed the corresponding values for the equations $\nu C{=}O = \rho\sigma^+ + a$, i.e, the values of ρ, the coefficients of correlation r, standard deviations S_0 of the free terms a, and the number of points n.

According to Student's test [6], in the 95% confidence interval, the difference found in values of ρ is not significant; this indicates an identical character of the influence of X in all of the series that are represented. A comparison of the coefficients ρ shows that the transmission factor of the pyrrole ring, which acts as a bridge grouping, is close to unity ($\pi' = \rho_I/\rho_{II} = 0.97$). Hence it follows that the pyrrole ring does not weaken the influence of X on the reaction center, and the existence of a correlation between $\nu C{=}O$ and the σ^+ constants is evidence of direct polar conjugation in the ground state between the substituent in the benzene ring and the electron-deficient COOH group, through the mechanism



A similar interaction in the ground state was established in [7] by means of dielectric constant measurements on molecules of 2-aryl-5-trifluoroacetylpyrroles, for which the magnitudes of the dipole moments correlated with the σ^+ constants of X in the benzene ring.

On the basis of literature data on the frequencies $\nu C{=}O$ in the IR spectra, we have made an attempt to evaluate the conduction of electronic effects by the pyrrole ring in comparison with the benzene ring. The question of whether the Hammet equation is applicable to pyrrole compounds was examined in [8]. It was shown that the frequencies of the stretching vibration $\nu C{=}O$ in the IR spectra of 2-substituted 3,4-dimethyl-5-carboethoxypyrroles correlate with the σ_p constants.

$$\nu_{C=O} = 1715 + 22.8\,\sigma_p$$
$$(r = 0{,}990;\ s_0 = 2.2;\ n = 5;\ \text{substituents: H, Me, I, CHO, } NO_2).$$

However, as we established, the use of the electrophilic constants for this series improves the quality of the correlation

$$\nu_{C=O} = (1716 \pm 0{,}17) + (20{,}2 \pm 0{,}4)\,\sigma^+$$
$$(r = 0{,}998;\ s_0 = 0{,}35).$$

TABLE 3. Charges and Bond Orders in Fragment $C^1-C^2(O^4)-O^3$

X	$p_{1,2}$	$p_{2,3}$	$p_{2,4}$	q_2	q_3	q_4
Benzoic acids						
H	0,9367	1,8203	1,0375	0,3398	-0,3034	-0,2837
MeO	0,9420	1,8158	1,0353	0,3458	-0,3087	-0,2863
Me	0,9366	1,8212	1,0356	0,3412	-0,3037	-0,2864
Cl	0,9336	1,8252	1,0383	0,3403	-0,2977	-0,2825
I	0,9326	1,8243	1,0403	0,3377	-0,2972	-0,2805
NO_2	0,9252	1,8316	1,0455	0,3350	-0,2854	-0,2742
2-Pyrrolecarboxylic acids						
H	0,9490	1,7979	1,0450	0,3705	-0,3202	-0,2765
MeO	0,9569	1,7905	1,0428	0,3734	-0,3265	-0,2771
Me	0,9499	1,7973	1,0431	0,3707	-0,3210	-0,2782
I	0,9402	1,8056	1,0533	0,3678	-0,3110	-0,2724
NO_2	0,9236	1,8214	1,0553	0,3627	-0,2906	-0,2633
2-Arylpyrrole-5-carboxylic acid						
H	0,9789	1,7480	1,0508	0,3780	-0,3829	-0,3028
MeO	0,9799	1,7460	1,0506	0,3783	-0,3844	-0,3032
Me	0,9804	1,7448	1,0515	0,3780	-0,3859	-0,3011
Cl	0,9771	1,7492	1,0524	0,3775	-0,3814	-0,3024
NO_2	0,9711	1,7550	1,0553	0,3761	-0,3747	-0,2990

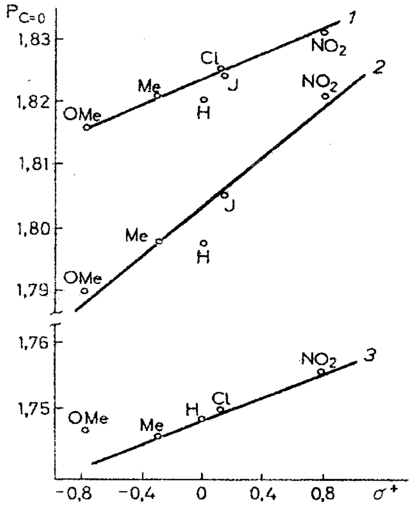


Fig. 1. C═O bond order in benzoic acids (1), 2-pyrrolecarboxylic acids (2), and 2-arylpyrrole-5-carboxylic acids (3) as a function of σ^+ constant of substituent.

From a comparison of the coefficients ρ in the equation and a comparison of the compounds V (Table 2), it can be seen that the pyrrole ring transmits the electronic effects of the substituents approximately twice as well as the benzene ring, probably because of its greater polarizability.

We have carried out a quantum-chemical calculation of the substituted benzoic acids I, 2-pyrrolecarboxylic acids II, and 2-arylpyrrole-5-carboxylic acids III. The calculated charges q_i and bond orders p_{ij} in the fragment $C^1-C^2(O^4)-O^3$ are listed in Table 3.

An analysis of these results shows that as the acceptor properties of the ring substituent are strengthened within each series, the orders of the C═O and C−O bonds increase, with a simultaneous decrease of $p_{1,2}$ of the ordinary C−C bond. Along with this, the magnitude of the negative charge on the carbonyl and carboxyl oxygen atoms decreases. The increase of multiplicity of the C═O bond is in accord with the experimentally observed increase of the νC═O frequency in the IR spectra. For all three series of compounds, the relationship between the calculated orders of the C═O bond and the charge on the carbonyl oxygen atom is expressed by the equation

$$p_{C=O} = 2{,}08 + 0.87\, q_3$$
$$(r = 0{,}994;\ s_0 = 0.0036;\ n = 16).$$

The lowering of frequency of the C═O stretching vibration when the change is made from the benzoic acids to the 2-arylpyrrole-5-carboxylic acids is consistent with the decrease of the C═O bond orders. The least squares method gives the relationship

$$\nu_{C=O} = 1078 + 365\, p_{C=O}$$
$$(r = 0.985,\ s_0 = 2.6,\ n = 10),$$

from which it is possible to predict values of νC═O in the pyrrolecarboxylic acids.

In the 2-arylpyrrole-5-carboxylic acids that we have studied, the variation of frequency of the C–O stretching vibration is determined mainly by the variation of the force constant of the C═O bond, which in turn is closely related to the order of this bond.

In Fig. 1 we show the calculated order of the C═O bond as a function of the σ^+ constant for the series of benzoic acids (1), 2-pyrrolecarboxylic acids (2), and 2-arylpyrrole-5-carboxylic acids (3). These straight lines are described by the following equations:

$$p_{C=O} = 1.8237 + 0{,}0099\,\sigma^+ \quad r = 0.994,\ s_0 = 0{,}0005; \tag{1}$$
$$p_{C=O} = 1.8032 + 0{,}0221\,\sigma^+ \quad r = 0.996,\ s_0 = 0{,}0009; \tag{2}$$
$$p_{C=O} = 1.7479 + 0{,}0091\,\sigma^+ \quad r = 0.994,\ s_0 = 0{,}0002. \tag{3}$$

The points for X = H are not included in the correlations (1) and (2). The numerical value of ρC═O in 2-(4-methoyphenyl)pyrrole-5-carboxylic acid (curve 3) is in poor agreement with the spectroscopic data, and the σ^+ constant for the OMe group was also excluded from the correlation. The transmission factors $\pi_2{}^1$ and $\pi_3{}^1$ that were calculated from Eqs. (1)-(3) are equal to 2.2 and 0.92, which are close to the corresponding values obtained on the basis of the IR spectroscopic data.

EXPERIMENTAL

The IR spectra of the 2-arylpyrrole-5-carboxylic acids were obtained in a Specord IR-75 spectrometer in tablets with KBr, and in CCl_4 solution (concentration 10^{-3} to $5 \cdot 10^{-5}$ M). The synthesis of the compounds was described in [9]. The quantum-chemical calculation was performed by the AM-1 method with complete optimization of geometry [10]. The starting geometry was taken from [11, 12].

REFERENCES

1. V. A. Pal'm Principles of Quantitative Theory of Organic Reactions [in Russian], Khimiya, Leningrad (1977).
2. Yu. A. Zhdanov and V. I. Minkin, Correlation Analysis in Organic Chemistry [in Russian], Izd. Rostov. Univ., Rostov-on-Don (1966).
3. J. W. Brooks, G. Erlinton, and J. F. Morman, J. Chem. Soc., No. 1, 106 (1961).
4. W. A. Seth-Paul and A. Van Duyse, Spectrochim. Acta, Part A, **28**, 211 (1972).
5. H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., **80**, 4979 (1958).
6. L. Z. Rumshinskii, Mathematical Treatment of Results of Experiments [in Russian], Nauka, Moscow (1971), p. 192.
7. B. A. Trofimov, V. B. Modonov, T. N. Akasamentova, A. I. Mikhaleva, S. E. Korostova, L. N. Sobenina, R. N. Nesterenko, and R. I. Polovnikova, Izv. Akad. Nauk. SSSR, Ser. Khim., No. 6, 1322 (1987).
8. L. I. Kazanskaya, T. A. Melent'eva, and V. M. Berezovskii, Zh. Obshch. Khim., **38**, 2020 (1968).

9. L. N. Sobenina, M. P. Sergeeva, A. I. Mikhaleva, M. V. Sigalov, S. E. Korostova, N. I. Golovanova, V. N. Salaurov, E. V. Bakhareva, and N. N. Vasil'eva, Khim. Geterotsikl. Soedin., No. 5, 612 (1990).
10. M. J. S. Dewar, E. G. Zoebish, E. F. Heali, and J. J. P. Stewart, J. Am. Chem. Soc., **107**, 3902 (1985).
11. K.-M. Marstokk and H. Mollendal, J. Mol. Struct., **23**, 93 (1974).
12. K. Orti, F. Tomas, and J. Sanchez-Marin, J. Mol. Struct., **104**, 197 (1983).