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Abstract

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VIBRATIONAL SPECTRA AND AROMATICITY OF SIX-MEMBERED AZACYCLES

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Many works in quantum chemistry are devoted to the calculation of force constants of molecules. However, quantum-chemical calculations, at any practically attainable accuracy, cannot serve to determine molecular force constants with an accuracy sufficient for calculating vibrational frequencies in proper agreement with experimental data. Therefore there remains only one way to determine force constants, namely, to calculate them from experimental values of frequencies and amplitudes of vibrations.

The force constants found by a semiempirical method are a quantitative characteristic of the properties of the electronic shells of molecules. Nevertheless, up to now the correlation between force constants and other parameters characterizing the electronic shell and the chemical behavior of a polyatomic molecule has scarcely been investigated. In the present work an attempt is made to establish such correlations.

Table 1

Diagonal influence coefficients of cyclohexane, benzene, and azacycles (in units of 10^{-6} cm^2)

Bonds and angles	Cyclohexane	Benzene	Pyridine	Pyrazine	*s*-Triazine	*s*-Tetrazine
CC	0,151	0,104	0,1070,105	0,106		
CN			0,101	0,103	0,104	0,105
NN						0,098
CH	0,127	0,117	0,117	0,117	0,117	0,117
CCC	0,653	0,355	0,3180,327			
NCC			0,334	0,337		
CNC			0,356	0,349	0,281	
CNN						0,281
NCN					0,290	0,271

Bonds and angles	Cyclohexane	Benzene	Pyridine	Pyrazine	*s*-Triazine	*s*-Tetrazine
CCH	1,012	0,793	0,7670,785	0,742		
NCH			0,786	0,737	0,745	0,726
HC out-of-plane*		2,333	2,304	2,406	2,848	
CC out-of-plane		3,268	2,415	2,463		
CN out-of-plane			1,667	1,869	2,778	

* Angles characterizing the out-of-plane displacement of CH, CC, and CN bonds from the plane of the ring.

From the mathematical point of view it is more expedient to establish relations not between force constants and other properties of molecules, but between the so-called influence coefficients and these properties, since the influence coefficients can be found in natural vibrational coordinates (1). The matrix of influence coefficients (i.c.) is the matrix inverse to the matrix of force constants. The mechanical meaning of the i.c. is as follows. Let R be the vector of changes in bond lengths and arcs during vibrations, and F the vector of generalized forces. In the small-vibration approximation $F = -KR$, where K is the matrix of force constants. The latter relation may be written in the form: $R = -K^{-1}F$; $K^{-1} = C$; C is the matrix of i.c. For a given force F, the displacement R is the smaller, the smaller C is. If C_{ii} is a diagonal element of the matrix C, then the corresponding bond or angle is the stronger, the smaller C_{ii} is. The interaction of vibrational coordinates R_i, R_j, the smaller the off-diagonal force constant C_{ij}. Thus, the elements of the matrix C serve as a quantitative characteristic of the strength and mutual influence of bonds. This role of force constants can be illustrated by comparing the force constants of cyclohexane, benzene, and azacycles (Table 1). The force constants of cyclohexane were determined by us from its force constants known from the work of Kuznetsova and Sushchinsky (2). The force constants of benzene and azacycles were calculated from the force constants of these molecules known from works (3,4). The calculation was carried out by inversion of the force-constant matrices. In Table 1 only the diagonal force constants of bonds and angles are indicated. From the data of this table it is clearly seen that the force constants of the CC, CN, NN, and CH bonds can characterize a bond just as well as bond orders. The angular force constants, reflecting the strengthening of angles in the series cyclohexane, benzene, pyridine, pyrazine, s-triazine, and s-tetrazine, serve as a quantitative measure of the change in strength in passing from cycloparaffins to aromatic hydrocarbons and further to heterocyclic aromatic compounds. The decrease in the force constants of pyridine in comparison with benzene reflects the greater stability of the pyridine ring, which apparently is also connected with the greater chemical stability of the pyridine system in comparison with the benzene system in a whole series of reactions, for example, under the action of nucleophilic agents (^{5}). The described properties of force constants indicate the advisability of comparing force constants with other quantitative characteristics of molecules. We shall characterize each carbon atom in pyridine by the sum of the diagonal force constants of the three angles with vertex at this atom:

$$\sum_{i=1}^{3} C_{ii}^{a}(\gamma, \beta) = \Sigma_a.$$

Fig. 1. Dependence of the sum of influence coefficients Σ_a on the value of the total charge Q_a on carbon atoms in pyridine

In Fig. 1 it is shown that, with increasing total charge of the carbon atom $Q_a = 1 - q_a$ (q_a is the π-electron charge) in pyridine, Σ_a also increases according to a linear law. The values of Q_a indicated in Fig. 1 were taken by us from Veselov’ s book (^{6}).

In Fig. 2 it is shown that, with increasing Σ_a for carbon atoms occupying different positions in the pyridine ring, the values of σ—the Hammett constants (^{7})—increase according to a linear law. This course of the σ values corresponds to an increase in the reactivity of the carbon atoms in the sequence meta-, ortho-, para-positions. Thus, the changes in Σ_a and σ are symbatic.

Fig. 2. Dependence of the Hammett σ-constant on the sum of influence coefficients Σ_a in pyridine

Let us now compare some properties of benzene and of the molecules of a series of azacyclic compounds. In Table 2 are compared: 1) the frequencies of totally symmetric deformation vibrations of the ring; 2) the sums of the diagonal force constants of all six internal angles of the ring

$$\sum_{a=1}^{6} C_{ii}^{a}(\gamma) = \Sigma_r$$

and 3) the sums of the π-electron populations of all six atoms $\sum_a q_a$, calculated by Peacock (^{8}).

From the data of Table 2 it is seen that in the sequence benzene, pyridine, diazi-

for triazine and tetrazine, the vibrational frequency increases regularly with decreasing value of Σ_r and with increasing sum of the π-electron populations.

From these data one may conclude that the ring is strengthened in the series under consideration.

The totality of the chemical and physical properties of the indicated azacyclic compounds determines their belonging to the class of aromatic compounds. Undoubtedly, the physical properties of aromatic compounds must also include the totality of dynamic characteristics—the influence coefficients. However, as shown in the works of Kursanov and Vol' pin ([9], [10]), no one of such properties taken separately can serve as a sufficiently strict criterion of aromaticity. The principal indication of aromaticity is considered to be the presence of a closed system of π-electrons, with which the entire set of physical and chemical properties of aromatic compounds is associated. In view of the universality of such a definition, it cannot serve to describe the differences of one aromatic compound from another.

Table 2

Comparison of the frequencies of totally symmetric deformation vibrations of rings, sums of angular influence coefficients, sums of π-electron populations of ring atoms, and aromaticity constants

Molecule	Frequency, cm^{-1}	Σ_r	$\sum_a q_a$ ([8])	K ([11])
Benzene	606	2.130	4.548	0
Pyridine	605	1.987	4.650	+23
Pyrazine	609	2.046	4.728	+46
Pyrimidine	624	–	4.732	+46
Pyridazine	619	–	4.706	+46
s-Triazine	675	1.713	4.802	+69
s-Tetrazine	737	1.666	–	+92

Only the identification of specific differences can serve as a basis for comparing aromatic compounds with one another. In Table 2 the values of Σ_r are compared with the aromaticity constants K, taken from the work of Balaban and Simon ([11]). A positive value of K corresponds to the ease of occurrence of a reaction with a nucleophilic reagent, while a negative value of K corresponds to the ease of occurrence of a reaction with an electrophilic reagent. From the data of Table 2 it is seen that the values of K increase regularly as Σ_r decreases, i.e., as the strength of the ring increases.

From all the results and comparisons of the present work the main conclusion follows: the influence coefficients, in particular the sum of the diagonal i.c. of the internal angles of the ring of six-membered aromatic compounds, may serve as one of the quantitative constants of aromaticity.

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CITED LITERATURE

1. L. S. Mayants, *Tr. Fiz. inst. im. P. N. Lebedeva AN SSSR*, **5**, 65 (1950).
2. T. I. Kuznetsova, M. M. Sushchinskii, *Optics and Spectroscopy*, collected papers, **2**, 1963, p. 144.
3. M. A. Kovner, A. M. Bogomolov, *Optics and Spectroscopy*, **4**, 301 (1958).
4. V. I. Berezin, *Optics and Spectroscopy*, **15**, 310 (1963).
5. *Pyridine and its Derivatives*, Part 1, N. Y.–London, 1960.
6. M. G. Veselov, *Elementary Quantum Mechanics of Atoms and Molecules*, 1962.
7. R. Daudel, R. Lefevre, C. Moser, *Quantum Chemistry*, London, 1959.
8. T. E. Peacock, *J. Chem. Soc.*, **1960**, 1946.
9. M. E. Vol' pin, *Uspekhi Khimii*, **29**, 298 (1960).
10. D. N. Kursanov, M. E. Vol' pin, *Journal of the All-Union Chemical Society named after D. I. Mendeleev*, **7**, 282 (1962).
11. A. T. Balaban, Z. Simon, *Tetrahedron*, **18**, 315 (1962).

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