treatment of 2.5 g (0.01 mole) of the compound (IIa) with powdered NaOH (0.02 mole) in abs. ether leads to the isolation of 2-methylcyclopenta[b]dihydrofuran (IVa) which is completely identical with the product obtained by the mercury-cyclization of 2-propargylcyclopentanol [3].

2-(Iodomethyl)-6a-methylcyclopenta[b]tetrahydrofuran (IIb). This compound was obtained by the iodination of the alcohol (Ib). The yield was 87%. The product has the bp 96-98°C (2 mm of Hg stem) and the n_D^{20} 1.5308. Found, %: C 40.9; H 5.4; I 48.0. $C_9H_{15}IO$. Calculated, %: C 40.6; H 5.7; I 47.7. The IR spectrum is characterized at 1095 cm^{-1} (C—O—C).

2-(Piperidinomethyl)-6a-phenylcyclopenta[b]tetrahydrofuran (IIIc). This compound was obtained by the iodination of 3.0 g (0.015 mole) of the alcohol (Ic) and the subsequent treatment of the furan (IIc) with the solution of 2.56 g (0.03 mole) of piperidine in benzene for 3 h at 80°C. The mixture is cooled, and the precipitated piperidine hydriodide salt is filtered off prior to the evaporation of the filtrate and distillation. The yield of the compound (IIIc) was 75%. The product has the bp 140-142°C (2 mm of Hg stem) and the n_D^{23} 1.5389. Found, %: C 79.8; H 9.3; N 5.1. $C_{19}H_{27}NO$. Calculated, %: C 80.0; H 9.5; N 4.9.

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ELECTRON STRUCTURES AND 13C NMR SPECTRA OF 3-SUBSTITUTED COUMARIN DERIVATIVES

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Quantum-chemical calculation of the electron densities on the atoms and the Wiberg indexes in coumarin and 3-amino-3-hydroxy-, and 3-carboxycoumarin molecules within the CNDO/2 approximation was accomplished. The 13C NMR spectra of the indicated compounds were recorded. The effect of the nature of the substituent in the pyrone ring on the electron structures of 3-substituted coumarin derivatives was evaluated on the basis of the data obtained. The character and degree of the relationship between the chemical shifts and the electron densities on the carbon atoms were established by means of regression analysis.

Coumarins are included among natural organic compounds that have diverse biological activity [1].

The chemical properties of coumarins have been studied rather fully [1, 2]. Attempts have been made to provide a basis for the reactivities of a number of coumarin derivatives from the results of quantum-chemical calculations by the Hückel [3] and Pariser—Parr—Pople (PPP) methods [4]. Some correlations between the calculated reactivity indexes and the

TABLE 1. Wiberg Indexes of Coumarin and Its Derivatives

| Bond	Coumarin	I	II	III
$O_{(1)}-C_{(2)}$	0,963	0,977	0,982	0,952
$C_{(2)}-C_{(3)}$	1,119	1,100	1,102	1,089
$C_{(3)}-C_{(4)}$	1,742	1,686	1,682	1,614
$C_{(5)}-C_{(6)}$	1,476	1,474	1,474	1,484
$C_{(6)}-C_{(7)}$	1,422	1,424	1,424	1,414
$C_{(7)}-C_{(8)}$	1,455	1,452	1,452	1,456
$C_{(8)}-C_{(9)}$	1,460	1,418	1,418	1,412
$C_{(9)}-C_{(10)}$	1,332	1,333	1,330	1,319
$C_{(10)}-O_{(11)}$	1,795	1,805	1,799	1,832
$C_{(9)}-O_{(1)}$	1,013	1,008	1,004	1,026
$C_{(3)}-R$	—	1,042	0,988	0,958

TABLE 2. Electron Densities on the Carbon Atoms and Chemical Shifts (δ, ppm) in the ^{13}C NMR Spectra of Coumarin and Its 3-Substituted Derivatives*

Compound	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(11)}$
I	(3,613) 158.82	(3,948) 133,34	(4,016) 125,38	(3,992) 108,04	(4,009) 124,46	(3,980) 124,84	(4,005) ·115,47	(3,839) 148,04	(4,001) 121,86	—
II	(3,624) 158.42	(3,917) 141,73	(4,017) 127,62	(3,990) 115,02	(4,009) 124,56	(3,980) 126,35	(4,016) 115,62	(3,839) 149,15	(4,003) 120,64	—
III	(3,655) 157,10	(4,121) 118,12	(3,886) 148,60	(3,963) 134,41	(4,016) 124,96	(3,972) 130,34	(4,043) 116,29	(3,802) 154,61	(4,037) 118,29	(3,642) 164,14
Coumarin	(3,579) 159,70	(4,176) 115,97	(3,917) 143,73	(3,975) 128,11	(4,018) 124,11	(3,965) 131,56	(4,065) 115,97	(3,816) 153,31	(4,028) 118,51	—

*The assignments were made in accordance with [11-14].

experimental principles in electrophilic, nucleophilic, and radical substitution reactions have been established [3].

Data on the electron structures of 3-substituted coumarins, particularly 3-amino- (I), 3-hydroxy- (II), and 3-carboxycoumarin (III), are not available in the literature, whereas these compounds, which contain several electron-donor atoms, are of interest as ligands for obtaining biologically and catalytically active complexes [5-7].
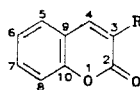
I – III

I R = NH₂, II R = OH, III R = COOH

We have performed quantum-chemical calculations of the electron densities on the atoms and the Wiberg indexes of coumarin and its 3-substituted derivatives I-III within the CNDO/2 approximation by means of the GEOMO program [8].

Considering the fact that the chemical shifts in the ^{13}C NMR spectra can serve as a measure of the magnitude of the electron density on the carbon atom, we obtained the ^{13}C NMR spectra of the indicated compounds and, on the basis of them, attempted to evaluate the effect of the nature of the substituent in the pyrone ring on the electron structures of 3-substituted coumarin derivatives.

In the calculation of the electron structures within the CNDO/2 approximation of coumarin and 3-substituted coumarins the geometries of the molecules were selected in accordance with the results of x-ray diffraction analysis of the compounds, which contain a pyrone ring [9]. The Wiberg indexes of the bonds in coumarin and its derivatives I-III are presented in Table 1. The values of these indexes indicate sesqui order of the bonds in the benzene ring; the C=O and $C_{(3)}=C_{(4)}$ bonds in the pyrone ring have clearly expressed double-bond character, while the remaining bonds can be characterized as single bonds. The data obtained are in good agreement with the behavior of the $C_{(3)}-C_{(4)}$ bond in photodimerization reactions and the diene synthesis, which proceed in complete conformity with the

TABLE 3. Parameters of the Empirical Mathematical Model

Parameters	Positions of the carbon atoms								
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$
q_1	3.6178	4.0402	3.9593	3.9798	4.0129	3.9742	4.0446	3.824	4.0171
b_0	158.51	127.29	136.33	121.41	124.52	128.27	115.84	151.28	119.83
b_1	−34.038	−94.741	−170.58	−857.3	−7.907	−430.16	−392.87	−170.94	−91.278

Woodward—Hoffmann rules of orbital symmetry [10]. In particular, coumarin, like maleic anhydride, adds butadienes at the double bond of the pyrone ring via a type of Diels—Alder reaction with the formation of a cyclic system [1].

The introduction of substituents such as NH_2 and OH into the 3 position of the pyrone ring leads to slight redistribution of the electron density in the coumarin molecule (Table 2). The carboxy group in III perturbs the coumarin π system to a greater extent than amino and hydroxy groups; this leads to a decrease in the orders of the $C_{(3)}$—$C_{(4)}$ bonds of the pyrone ring in derivative III as compared with unsubstituted coumarin. One should note the decrease in the electron density on the oxygen atom of the carbonyl group of the III molecule. This is possibly a consequence of the formation of an intramolecular hydrogen bond between the carboxy group and the carbonyl oxygen atom in this compound. The electron density on the carbon atoms remains virtually unchanged.

The chemical shift of the carbon atom of benzene and the increments of the amino, hydroxy, and carboxy groups [11] were used as the starting values in the assignment of the chemical shifts of the carbon atoms in the ^{13}C NMR spectra of 3-substituted coumarins. We also compared the spectra and assignments that we obtained with the ^{13}C NMR spectra of unsubstituted coumarin [12, 13] and its 3-bromo-substituted derivative [14]. The assignment of the signals to the corresponding carbon atoms for each of the compounds was accomplished on the basis of the spectra with incomplete proton decoupling (Table 2).

As a result of analysis of the spectra it was established that when NH_2 and OH groups are introduced into the 3 position the greatest chemical shift to weak field as compared with unsubstituted coumarin is observed for the $C_{(3)}$ atom ($\Delta\delta$ 18 and 26 ppm, respectively), while the signals of the $C_{(4)}$ and $C_{(5)}$ atoms are shifted to strong field [$\Delta\delta C_{(4)}$ 18 and 16 ppm, $\Delta\delta$ $C_{(5)}$ 20.13 and 13.09 ppm]. The weak shift of the signals of the remaining carbon atoms should be noted.

A different pattern is observed when a COOH group is introduced into the 3 position. The chemical shift of all of the carbon atoms in the III molecule is rather weak as compared with coumarin and does not exceed 6.3 ppm for $C_{(5)}$.

A comparison of the ^{13}C NMR spectra of 3-substituted coumarins with the results of calculations of the electron structures of these molecules enabled us to uncover a rectilinear relationship between the chemical shifts and the electron densities on the corresponding carbon atoms of the investigated compounds. A similar relationship was previously established [15] for coumarin and protonated coumarin calculated within the CNDO/2 approximation.

Thus, the chemical shifts in the ^{13}C NMR spectra convey the distribution of the electron density within the limits of the indicated series of compounds and thereby make it possible to evaluate the relative change in the distribution of the electron density when a substituent is introduced into the pyrone ring of coumarin derivatives.

A regression method [16] was used to establish the character of the relationship between the chemical shift δ and the electron density q.

An empirical mathematical model of the following form was constructed for the compounds obtained and analyzed thoroughly:

$$\delta = \beta_0 + \beta_1 (q - \bar{q}),$$

where $\bar{q}$ is a random average value. Unshifted estimates b_0 and b_1 of the β_0 and β_1 parameters are obtained by the method of least squares. The q, b_0, and b_1 values are presented in Table 3.

Regression analysis leads to the following results. The mathematical model is adequate for the $C_{(2)}$ and $C_{(6)}$–$C_{(10)}$ atoms with a significance level $\alpha = 0.05$, whereas for the $C_{(3)}$–$C_{(5)}$ atoms it is adequate when $\alpha = 0.01$. The b_1 coefficient of the empirical model for the $C_{(6)}$ atom was found to be statistically insignificant at significance level $\alpha = 0.05$.

The constructed mathematical model makes it possible to predict the chemical shifts for the $C_{(2)}$ and $C_{(6)}$–$C_{(10)}$ atoms with a relative error of no more than $5 \cdot 10^{-3}$, as compared with no more than $2 \cdot 10^{-2}$ for the $C_{(3)}$–$C_{(5)}$ atoms.

The inverted regression equation $q = \bar{q} + (\delta - b_0)/b_1$ can be used to calculate the electron densities on various carbon atoms of 3-substituted coumarin derivatives from the measured values of the chemical shifts; the relative error in the results of the calculation will not exceed $2 \cdot 10^{-3}$ for the $C_{(2)}$, $C_{(4)}$, $C_{(5)}$, $C_{(7)}$, and $C_{(10)}$ atoms and $1.5 \cdot 10^{-2}$ for the $C_{(3)}$ and $C_{(6)}$ atoms.

Thus, the statistical hypothesis regarding a linear dependence of the chemical shift on the electron density for the compounds obtained is accepted.

EXPERIMENTAL

The synthesis of the 3-substituted coumarin derivatives was accomplished by known methods [17, 18]. The ^{13}C NMR spectra of the investigated compounds were recorded with a Varian FT-80A spectrometer (80 MHz) and d_6-DMSO as the solvent. The concentration of the substances was 0.5 mole/liter. The chemical shifts were measured relative to an internal standard, viz., the signals of the carbon atoms of the solvent (39.6 ppm relative to TMS).

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