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REACTIONS OF 7-AMINOCOUMARINS LEADING TO ALKYLIDENEBENZOPYRANS

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UDC 547.814'587.51:543.422'51

The reaction of 7-aminocoumarins with triethyloxonium tetrafluoroborate leads to benzopyrylium salts that react with sodium derivatives of compounds that contain an active methylene group to give substituted 2-methylene-2H-1-benzopyrans. The structures and physicochemical properties of the synthesized compounds are discussed.

The molecules of 7-aminocoumarins contain several reaction centers that are subject to electrophilic attack: the nitrogen atom, the $C_{(3)}$, $C_{(6)}$, and $C_{(8)}$ atoms of the benzopyran fragment, and the exocyclic oxygen atom of the pyrone ring. We have previously investigated [1] a number of reactions of coumarins I and II with electrophiles that lead to the synthesis of C-substituted derivatives. It was shown that soft Lewis acids ($ZnCl_2$, $HgCl_2$) are capable of coordinating with the carbonyl group of 7-aminocoumarins and of leading to regiospecific substitution reactions in the 3 position. In this connection we became interested in the possibility of the selective modification of the carbonyl group by means of electrophilic addition reactions.

Taking into account the potential tendency of 7-aminocoumarin dyes for marked charge separation within the molecule [2, 3], replacement of the carbonyl oxygen atom by the $=C\begin{smallmatrix}\diagup X\\ \diagdown Y\end{smallmatrix}$ fragment seemed of particular interest for the transition to other strongly polarized structures. As a result, the aim of the present research was to develop a method for the synthesis of 2-methylene-2H-1-benzopyrans on the basis of aminocoumarins I-III.

Benzopyrylium salts and 2,2-dialkoxybenzopyrans [4-6] could be potential sources of methylenebenzopyrans, and we therefore initially evaluated methods for the generation of benzopyrylium salts on the basis of coumarins I-III. We found that the reaction of I-III with electropyilic reagents such as triethyloxonium tetrafluoroborate, dimethyl sulfate, and phosphorus oxychloride in solution in methylene chloride, chloroform, or benzene leads to the formation of aminobenzopyrylium salts (for example, Ia and IIa) in 80-95% yields. (Formula, top, following page.)

The reactions with triethyloxonium tetrafluoroborate proceed most smoothly. The ready formation of salts Ia and IIa is evidently a privilege of precisely 7-aminocoumarins, in which the amino group acts as an additional factor in the stabilization of the benzopyrylium system.

The aminobenzopyrylium salts are bright-yellow substances that are relatively stable in solution in CH_2Cl_2 but decompose rapidly in air. For identification, as an example we isolated tetrafluoroborate salt Ia (mp 136°C) and, despite unsuccessful attempts to obtain satisfactory results of elementary analysis, determined its physicochemical parameters. Thus signals of

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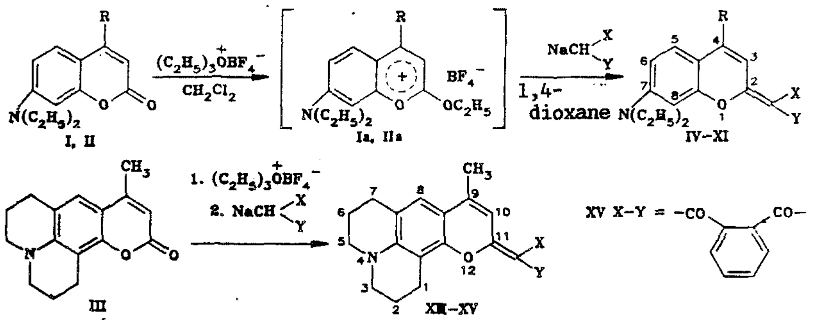


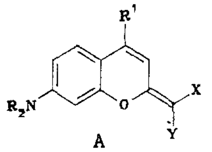
IV—IX R=CH_3, X, XI R=H; IV, XII X=Y=$COCH_3$, V, XIII X=Y=$CO_2C_2H_5$, VI X=Y= =CN, VII, X, XIV X=$COCH_3$, Y=$CO_2C_2H_5$, VIII, XI X=$CO_2C_2H_5$, Y=CN, IX X–Y= =—$COCH_2C(CH_3)_2CH_2CO$—

protons of an OCH_2CH_3 group are present in the PMR spectrum of salt Ia at 1.54 and 4.92 ppm. The signals of most of the protons of the benzopyran fragment are shifted 0.3-0.7 ppm to weak field as compared with the starting coumarin [7]. Intense absorption at 1060 cm^{-1}, which is characteristic for the BF_4^- anion, is observed in the IR spectrum of salt Ia. Vibrations of the C=C bonds of aromatic rings show up at 1620-1650 cm^{-1}. Considering the low stability of 7-aminobenzopyrylium salts it is expedient to carry out reactions with them without isolation and special purification.

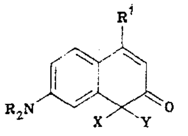
For the synthesis of methylenebenzopyrans the sodium derivatives of various compounds that contain an active methylene group, viz., acetoacetic and cyanoacetic esters, diethyl malonate, acetylacetone, malonic acid dinitrile, dimedone, and indan-1,3-dione, were subjected to reaction with the salts. As a result of heating of the reagents in dioxane we isolated methylenebenzopyrans IV-XV, the overall yields of which from the coumarins were 30-60% (see Table 1). Compounds IV-XV can be obtained in about the same yields by prior treatment of the benzopyrylium salts with an equivalent amount of sodium methoxide with subsequent heating of the reaction mixture with the corresponding methylene component. In this case the reaction evidently proceeds with the formation of intermediate 2,2-dialkoxy derivatives [6], as evidenced by the instant of decolorization of the reaction mixture.

Rather unexpectedly, the establishment of the detailed structures of IV-XV proved to be a difficult task. First of all, it was necessary to solve the problem of distinguishing the structures of methylenebenzopyrans (A) and possible isomers of the **B** and **C** type.

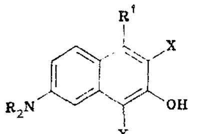
The correspondence of the synthesized compounds to the elementary compositions of isomers **A-C** was established in the case of XI by means of the high-resolution mass spectrum (see Table 1).



A



B



C

TABLE 1. Characteristics of IV-XV

Compound	mp, °C	R_f	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
IV	124	0,24	73,0	7,5	4,5	$C_{19}H_{23}NO_3$	72,8	7,4	4,5	40
V	116	0,32	67,9	7,2	4,1	$C_{21}H_{27}NO_5$	67,5	7,3	3,8	48
VI	201	0,27	73,4	6,3	14,6	$C_{17}H_{17}N_3O$	73,1	6,1	15,0	45
VII	84	0,27	70,3	7,7	4,2	$C_{20}H_{25}NO_4$	70,0	7,3	4,1	68
VIII	146	0,28	70,1	6,6	8,5	$C_{19}H_{22}N_2O_3$	70,0	6,8	8,6	76
IX	162	0,24	75,2	7,8	3,8	$C_{22}H_{27}NO_3$	74,8	7,7	4,0	38
X	79	0,26	69,2	7,2	4,2	$C_{19}H_{23}NO_4$	69,3	7,0	4,2	54
XI*	122	0,28				$C_{18}H_{20}N_2O_3$				58
XII	161	0,25	74,7	7,0	4,1	$C_{21}H_{23}NO_3$	74,7	6,9	4,2	42
XIII	216 dec.	0,31	69,4	6,8	3,9	$C_{23}H_{27}NO_5$	69,5	6,9	3,5	50
XIV	77	0,27	72,1	6,9	4,0	$C_{22}H_{25}NO_4$	71,9	6,9	3,8	70
XV	220 dec.	0,23	78,0	5,8	3,6	$C_{25}H_{21}NO_3$	78,3	5,5	3,7	23

*The compound was identified by means of the high-resolution mass spectrum. Found: M^+ 312.1495. $C_{18}H_{20}N_2O_3$. Calculated: M 312.1493.

TABLE 2. PMR Spectra of IV-XI, Chemical Shifts (δ, ppm) ($CDCl_3$), and Form of the Signal (J, Hz)*

Compound	3-H	5-H	6-H	8-H (d)	Substituent in 4 position	$(CH_3-CH_2)_2N$		Other protons**
						CH_3 (t)	CH_2 (q)	
IV	7,48 s	7,32 d (9,0)	6,59 dd (9,0; 2,5)	6,35 (2,5)	2,30 s	1,21 (7,0)	3,41 (7,0)	2,42 (6H, s, $2CH_3CO$)
V	7,43 s	7,24 d (8,9)	6,50 dd (8,9; 2,2)	6,32 (2,2)	2,27 s	1,17 (6,9)	3,37 (6,9)	1,28 (3H, t, $\mathbf{CH_3}CH_2O$), 1,37 (3H, t $\mathbf{CH_3}CH_2O$), 4,21 (2H, q $CH_3\mathbf{CH_2}O$), 4,35 (2H, q, $CH_3\mathbf{CH_2}O$)
VI	6,51 s	7,43 d (9,1)	6,69 dd (9,1; 2,3)	6,56 (2,3)	2,40 s	1,22 (7,0)	3,45 (7,0)	
VII	—	7,35 d (9,0)	6,63 dd (9,0; 2,5)	6,38 (2,5)	2,30 s	1,16 (7,0)	3,43 (7,0)	1,32 (3H, t, J=6,9, $\mathbf{CH_3}CH_2O$), 2,22 (3H, s, CH_3CO), 4,42 (2H, q, J=6,9, $CH_3\mathbf{CH_2}O$)
VIII	7.73	7,45 d (9,2)	6,73 dd (9,2; 2,4)	6,54 (2,4)	2,41 s	1,21 (7,1)	3,46 (7,1)	1,34 (3H, t, $\mathbf{CH_3}CH_2O$), 4,23 (2H, q $CH_3\mathbf{CH_2}O$)
IX	8,30 q (1,0)	7,49 d (9,1)	6,75 dd (9,1; 2,4)	6,76 (2,4)	2,48 d (1,0)	1,22 (7,0)	3,45 (7,0)	1,09 (6H, s, $2CH_3$), 1,09 (4H, s $2CH_2CO$)
X	—	7,07 d (9,0)	6,46 dd (9,0; 2,3)	6,29 (2,3)	7,15 s	1,14 (7,0)	3,34 (7,0)	1,35 (3H, t, J=7,0, $\mathbf{CH_3}CH_2O$), 2,33 (3H, s, CH_3CO), 4,31 (2H, q, J=7,0=$CH_3\mathbf{CH_2}O$)
XI	8,08 d (9,5)	7,39 s	7,39 d (2,3)	7,0 (2,3)	7,41 d (9,5)	1,22 (7,0)	3,44 (7,0)	1,35 (3H, t, $\mathbf{CH_3}CH_2O$), 4,28 (2H, q, $CH_3\mathbf{CH_2}O$)

*The number of the atoms is presented in the first scheme; this is also the case for Table 3.

**For V, VIII, and XI J = 7.0 Hz.

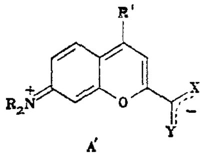
TABLE 3. PMR Spectra of XII-XV, Chemical Shifts (δ, ppm) ($CDCl_3$), and Form of the Signal (J, Hz)

Compound	1-H (t)	2-H (m)	3-H (t)	5-H (t)	6-H (t)	7-H (t)	8-H (s)	9-CH_3 (s)	10-H (s)	Other protons*
XII	2,76 (5,9)	1,95	3,24 (5,8)	3,26 (5,8)	1,95	2,79 (5,9)	6,92	2,29	7,51	2,39 (6H, s, $2CH_3CO$)
XIII	2,69 (6,0)	1,92	3,24 (5,9)	3,27 (5,9)	1,92	2,74 (6,0)	6,99	2,28	7,33	1,22 (3H, t, $\mathbf{CH_3}CH_2O$), 1,28 (3H, t, $\mathbf{CH_3}CH_2O$), 4,12 (2H, q, $CH_3\mathbf{CH_2}O$), 4,21 (2H, q, $CH_3\mathbf{CH_2}O$)
XIV	2,76 (6,2)	1,95	3,22 (6,0)	3,24 (6,0)	1,95	2,79 (6,2)	6,95	2,28	7,58	1,34 (3H, t, J=7,1, $\mathbf{CH_3}CH_2O$), 2,31 (3H, s, CH_3CO), 4,30 (2H, q, J=7,1, $CH_3\mathbf{CH_2}O$)
XV	3,25 (6,2)	2,00	3,30 (6,1)	3,33 (6,1)	2,00	2,79 (6,2)	7,06	2,48	7,97	7,55 (2H, dd, meta arom. 7,72 (2H, dd ortho arom.)

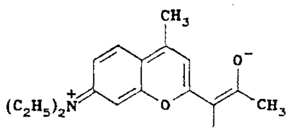
*For XIII J = 7.0 Hz, while J_1 = 8.5 Hz and J_2 = 2.3 Hz for XV.

It was observed that IV, V, VII, X, and XII-XIV give an intense red coloration with a methanol solution of ferric chloride. In principle, this fact does not exclude the existence of isomers of the **C** type for these substances. Instead of a signal at 5.5-6.0 ppm, which corresponds to the 3-H proton in the starting coumarins, the PMR spectra of IV, V, VIII, IX, and XI-XV contain a single signal of a lone proton at 7.3-8.3 ppm (see Tables 2 and 3). Of particular interest are the PMR spectra of chloroform solutions of VII and X, in which signals corresponding to the 3-H proton are completely absent, while the signals of the protons of methyl and ethyl groups of the acetoacetic ester fragment (2.2-2.3 and 1.3 ppm; 4.3-4.4 ppm, respectively) are markedly broadened. At the same time, the signals of the remaining protons in VII and X are retained distinctly and are located in positions similar to those for the other compounds IV-VI, VIII, IX, and XI-XV. This fact may constitute evidence for a certain dynamic process and also, in principle, does not contradict structures of the **C** type, in which an intramolecular hydrogen bond with rapid exchange of a proton between two functional groups is possible. However, the formation of such substances seems unlikely for cyclic 1,3-diketones. In addition, in the case of the **C** isomers the monotypic groups (X = Y) for symmetrically substituted compounds have different chemical environments, and the signals of the alkyl protons of these groups in the PMR spectra should not coincide even in the case of rapid reorientation of the hydrogen bond. However, this is not so for IV, IX, and XII (see Tables 2 and 3), and, consequently, the spatial orientation of the X and Y groups should be symmetrical. In principle, isomers of the **B** type satisfy this condition. In addition, the reason for the weak-field shift of the 3-H signals in the PMR spectra is not clear for the **B** isomers. In this case it is also difficult to explain the appearance of a long-wave absorption band (λ_{max} 440-520 nm) in the electronic spectra of IV-XV (Table 4). Finally, the absorption band of an additional carbonyl group that is expected for the **B** isomers cannot be exposed in the IR spectra of the synthesized substances.

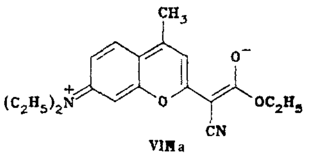
Thus, at first glance, the spectral data constitute evidence for the nonmonotypic character of structures IV-XV. Nevertheless, a reasonable interpretation can still be given to the observed facts if it is assumed that IV-XV exist in the form of isomers of the **A** type; rapid rotation of the CXY fragment about the exocyclic C=C bond may occur in solution. In fact, in methylenebenzopyrans IV-XV one should expect marked intramolecular charge separation, which is reflected by limiting structure **A'**.



A'



VIIa



VIIIa

In this case rotation about the exocyclic C=C bond should be facilitated, and the signals of the protons of the X and Y groups in the PMR spectra may be broadened (see the spectra of VII and X) or averaged on the NMR time scale. In analogy with alkylidenepyrans [8], the weak-field shift of the 3-H signal is a consequence of the drawing together in space of this proton and the functional group. The formation of a coloration with ferric chloride solution also becomes explainable, since in the **A'** form IV, V, VII, X, and XII-XIV are capable of giving charge-transfer complexes (CTC) or even salt products of the $[Fe(OR)_mCl_n]^{m+} \cdot mCl^-$ type, where m + n = 3, and R is an organic cation fragment.

The high polarization of structures IV-XV should lead to a bathochromic shift of the absorption bands and emission in the electronic spectra, and this is actually observed (see Table 4). The bathochromic shift increases successively in the order $CO_2C_2H_5$ < CN < $COCH_3$ for the X and Y substituents for the examined compounds. This regularity evidently reflects the superimposition of two tendencies that promote intramolecular charge separation — an increase in the electron-acceptor character of the substituent (which is maximal for the acetyl group) and a decrease in steric hindrance (which is minimal for the nitrile group), which disrupts the planarity of the conjugation chain. Since intramolecular charge separation models, as it were, a "pre-excited" state, the luminescence quantum yields decrease markedly for methylenebenzopyrans as compared with the starting coumarins I-III [9].

For the definitive elucidation of the structures of the synthesized substances we recorded the low-temperature PMR spectra of VII and conducted an x-ray diffraction study of VII and VIII.* The data obtained confirmed that IV-XV exist in the **A** form with marked charge separation, which makes the structure of the methylenebenzopyrans close to the quinoid structure (**A'**).

Yet another conformational problem for unsymmetrically substituted VII, VIII, X, XI, and XIV is the determination of the orientation of the X and Y groups relative to the exocyclic C=C bond. It might be assumed that a configuration of the X and Y groups in which the group that is a better π acceptor is closer to the direction of charge transfer is more favorable [10]. In the designations presented above the X group satisfies this condition. In fact, the x-ray diffraction data showed that in the crystalline state VII exists in the VIIa form (see above), in which the better acceptor — the acetyl group — is situated in the plane of the aromatic fragment and occupies the X position, while the carbethoxy group deviates from the indicated plane. On the other hand, in VII the carbethoxy group — a better electron-acceptor group as compared with the nitrile group (see structure VIIIa) — is found in the X position. To solve the problem of the preferred orientation of the X and Y groups in solution one can use PMR spectroscopic data (see Table 3). Thus the chemical shifts of the 3-H proton in VIII

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*This part of the research was carried out jointly with D. S. Yufit and Yu. T. Struchkov and will be published separately.

TABLE 4. IR and UV Spectra of IV-XV

Compound	IR spectrum in KBr, ν, cm^{-1}		UV spectrum (in ethanol), λ_{max}, nm (log ε)
	C≡N, C=O	C=C	
IV	1690	1640	257 (4,58), 278 (4,32), 460 (4,59), 481 (4,62)
V	1720, 1700	1640	252 (4,48), 273 (4,10), 283 (4,01), 320 (3,60), 408 (4,36), 426 (4,45), 443 (4,39)
VI	2210	1630	247 (4,30), 253 (4,39), 272 (4,19), 278 (4,21), 450 (4,41), 475 (4,50)
VII	1700	1645	245 (4,58), 272 (4,21), 304 (3,84), 322 (3,74), 448 (4,55), 472 (4,55)
VIII	2210, 1695	1645	251 (4,60), 276 (4,37), 334 (3,83), 346 (3,74), 448 (4,12), 474 (4,71)
IX	1620	1590	257 (4,56), 274 (4,50), 305 (3,88), 360 (3,90), 495 (5,06)
X	1690	1640	256 (4,43), 274 (4,01), 4,56 (4,44), 480 (4,40)
XI	2210, 1700		246 (4,11), 253 (4,24), 273 (4,05), 376 (4,14), 462 (4,15), 490 (4,21)
XII	1675	1630	218 (4,25), 264 (4,34), 288 (4,17), 314 (3,84), 467 (4,38), 498 (4,90)
XIII	1725, 1690	1640	252 (4,46), 274 (4,08), 287 (3,99), 328 (3,58), 410 (4,31), 431 (4,42), 450 (4,34)
XIV	1700	1640	262 (4,53), 276 (4,30), 308 (3,98), 324 (3,77), 463 (4,60), 487 (4,64)
XV	1630	1580	230 (3,76), 248 (3,90), 267 (3,88), 292 (3,69), 380 (3,39), 524 (4,17)

and XIV may be close to the analogous shifts for V and XIII, respectively. In this case the $CO_2C_2H_5$ group in the VIII and XIV molecules should preferably occupy the X position or have an analogy with VI (for VIII) and XII (for XIV), and the orientation of the X and Y substituents should then be the opposite. The data in Table 2 indicate an analogy in the PMR spectra for V and VIII, as well as for XII and XIV; this is in agreement with the results of x-ray diffraction analysis and for the unsymmetrically substituted compounds ($X \neq Y$) confirms the presence in solution of primarily conformers that correspond to structures VII, VIII, X, XI, and XIV.

EXPERIMENTAL

The IR spectra (KBr pellets) were obtained with a Jasco IR-S spectrometer. The UV spectra were recorded with a Hitachi EPS-3T spectrophotometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Bruker WM spectrometer (250 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with a Varian MAT-311A mass spectrometer (ionizing voltage 70 eV).

The reaction products were isolated by chromatography with a column (30 by 2.5 cm) packed with Silpearl UV-254 silica gel in a hexane—acetone system (3:1). The purity of the substances was monitored by means of TLC on Silufol UV-254 plates in the same system. The physicochemical characteristics of the synthesized IV-XV are presented in Table 1.

2-Ethoxy-4-methyl-7-diethylaminobenzopyrylium Tetrafluoroborate (Ia). A mixture of 1.15 g (5 mmole) of coumarin I and 0.94 g (5 mmole) of triethyloxonium tetrafluoroborate in 15 ml of dry CH_2Cl_2 was stirred at 20°C for 40 min in an inert atmosphere, after which 25 ml of absolute ether was added. The resulting precipitate was removed by filtration in an inert atmosphere and dried in vacuo to give 1.43 g (90%) of Ia with mp 136°C (dec.). IR spectrum (KBr) 1060 (BF_4^-), 1620, 1640, 1650 cm^{-1} (C=C). PMR spectrum ($CDCl_3$): 1.23 (6H, t, J = 7.0 Hz, $2NCH_2\mathbf{CH_3}$), 1.54 (3H, t, J = 7.0 Hz, $OCH_2\mathbf{CH_3}$), 2.52 (3H, s, 4-CH_3), 3.65 (4H, q, J = 7.0 Hz, $2N\mathbf{CH_2}CH_3$), 4.92 (2H, q, J = 7.0 Hz, $O\mathbf{CH_2}CH_3$), 6.35 (1H, d, J = 2.2 Hz, 8-H), 6.62 (1H, s, 3-H), 6.92 (1H, dd, J_1 = 9.0 Hz, J_2 = 2.2 Hz, 6-H), 7.90 (1H, d, J = 9.0 Hz, 5-H).

General Method for Obtaining IV-XV. A mixture of 5 mmole of the corresponding coumarin I-III and 5 mmole of triethyloxonium tetrafluoroborate in 15 ml of dry CH_2Cl_2 was stirred at 20°C for 40 min in an inert atmosphere, after which the solvent was evaporated in vacuo. A solution (or suspension) of 10 mmole of the sodium derivative of the corresponding methylene component, obtained by the standard method [11], in 20 ml of dry dioxane was added to the residue, and the reaction mixture was stirred vigorously at 50°C for 4 h. It was then evaporated, and the residue was separated chromatographically. The isolated substances were recrystallized from hexane—acetone.

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STEREOSPECIFICITY OF SPIN-SPIN COUPLING CONSTANTS (SSCC) OF ^{1}H, ^{15}N, AND ^{19}F NUCLEI IN SUBSTITUTED 2,2-BIS(TRIFLUOROMETHYL)AZIRIDINES*

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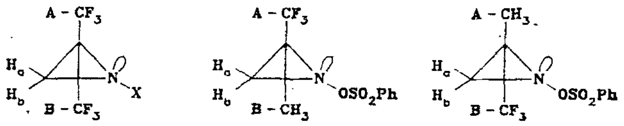
1-Chloro-, 3-methyl-, 1-chloro-3-cyano-, 1-carbomethoxymethoxy-3-methyl-, and 1-carboxymethoxy-3-methyl-2,2-bis(trifluoromethyl)aziridines were synthesized for the first time. Criteria for distinguishing cis- and trans-3-substituted and 1,3-disubstituted 2,2-bis(trifluoromethyl)aziridines from the parameters of the ^{1}H, ^{13}C, and ^{19}F NMR spectra were found.

Stereospecificity of the spin-spin coupling constants (SSCC) of the ring protons is observed in series of configurationally stable 2-methyl-2-trifluoromethyl- and 2,2-bis(trifluoromethyl)aziridines. Thus the long-range trans-SSCC with respect to the nuclei of CF_3 and CH_3 substituents ($^4J^{trans}$) is always greater for the H_a proton, which is cis-oriented relative to the unshared electron pair (UEP) of the ring N atom [2, 3]:



$^4J^{\text{trans}}_{B\text{-}CF_3H_a} > {}^4J^{\text{trans}}_{A\text{-}CF_3H_b}$ and $^4J^{\text{trans}}_{B\text{-}MeH_a} > {}^4J^{\text{trans}}_{A\text{-}MeH_b}$

It has been shown by theoretical calculations and experimental studies that the geminal SSCC of the N nucleus of the aziridine ring $^2J_{NH}$ is always greater with the cis proton with respect to the UEP of the N atom and amounts to ~10.5 Hz, while with the trans proton it does not exceed 1 Hz or is not observed at all [4].

For other aziridine derivatives it has been established that, regardless of the type of substituent in the ring, the vicinal SSCC of the ring protons $^3J^{cis}$ in the cis position relative to the UEP of the N atom is 1-2 Hz smaller than for the trans protons [5].

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