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BASICITY CONSTANTS OF ISOMERIC AZAFLUORENES AND THEIR DERIVATIVES

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Data are given for the first time on the measurement of basicity constants of the isomeric azafluorenes and their derivatives, which enable a study of the effect of this property on the relationship of the geometric isomers of substituted fluorenes and azomethines obtained from azafluorenes and their keto derivatives.

Keywords: azafluorenes, basicity constants.

Azafluorenes isomeric at the position of the nitrogen atom are of considerable interest in the search for biologically active compounds [1-4], as π ligand systems in syntheses of new π-complex compounds based on them, and also in the study of the mechanism of metallotropic rearrangements [5, 6]. Convenient heterogeneously catalyzed routes for obtaining azafluorenes developed in our laboratories [7] have assisted the development of the chemistry of these heterocycles and have enabled, in particular, systematic synthetic and stereochemical investigations to be carried out on arylidene and azomethine derivatives of azafluorenes [3, 4]. As a continuation of investigations of the effect of various factors on the relationship of the geometric isomers of arylidene and azomethine derivatives of azafluorenes [3, 4, 7] in the present work basicity constants have been measured for the first time for isomeric azafluorenes, azafluorenones, their methyl and nitro derivatives, and also methylcarbethoxy-containing 4-aza-9-fluorenone.

The basicity constants of compounds **1-21** were determined in ethanol solution by potentiometric titration with sulfuric acid in a SF-16 spectrophotometer operated manually. The degree of purity of the samples investigated was checked by TLC on Al_2O_3 of activity grade II and by IR and NMR spectroscopy. Mean values of the basicity constants of the samples investigated were found from the data of 4 to 15 determinations of this property for each sample (Tables 1, 2).

It is known [8, 9] that C-methylation of N-heterocycles and aromatic amines usually leads to an increase in the ionization constant (the exception is *meta* C-methylation occasionally). In the case of the nitrogen heterocycles (pyridine, quinoline, isoquinoline, etc.) the pK changes more significantly. The mean value of $\Delta pK = +0.7\text{-}0.8$ for one methyl group introduced [8-10].

The pK increases with an increase in the number of methyl groups introduced [8-10]. For example in the series pyridine, 2-picoline, 4-picoline, 2,6-lutidine, 2,4-lutidine, and 2,4,6-collidine the pK values are 5.23, 5.96, 6.05, 6.62, 6.79, and 7.45 respectively [10].

As is seen from Tables 1 and 2 the introduction of electron-donating substituents such as methyl into the azafluorene nucleus leads to a marked increase in the pK of these systems and this effect is more significant on introducing these substituents into the pyridine nucleus of an azafluorene or its keto derivative. Replacement of

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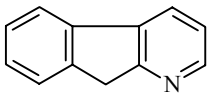
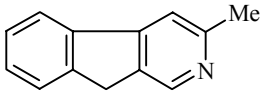


1-azafluorene **1**



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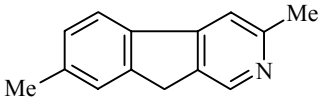

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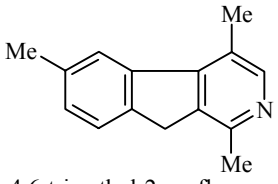

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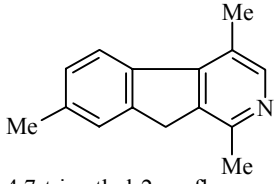
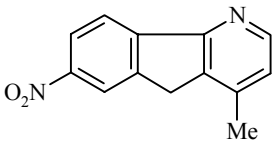
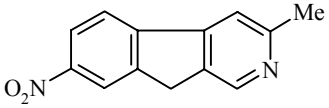


1,4,7-trimethyl-2-azafluorene **5**



1-methyl-7-nitro-4-azafluorene **6**



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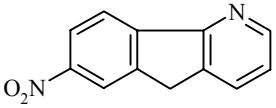
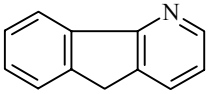


7-nitro-4-azafluorene **8**



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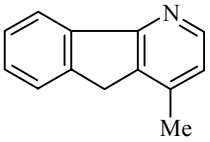

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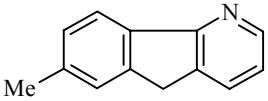

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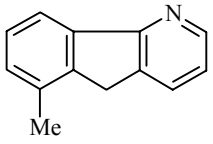

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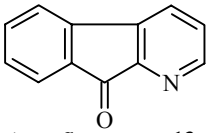
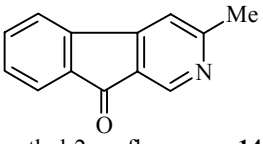


1-azafluorenone **13**



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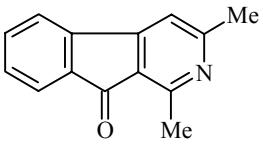
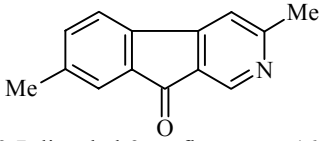
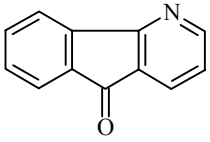


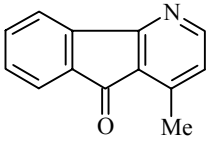
1,3-dimethyl-2-azafluorenone **15**



3,7-dimethyl-2-azafluorenone **16**



4-azafluorenone **17**



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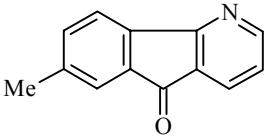
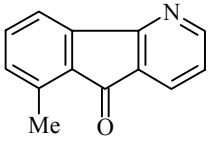
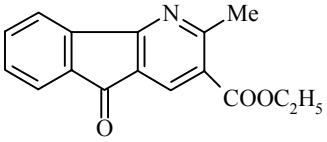


7-methyl-4-azafluorenone **19**



8-methyl-4-azafluorenone **20**



2-carbethoxy-3-methyl-4-azafluorenone **21**

the hydrogen atoms in position 9 of azafluorenes by an oxygen atom causes the opposite effect, and this influence is even more marked on introducing an electron-withdrawing substituent, such as a nitro or carbethoxy group, into azafluorene or azafluorenone.

TABLE 1. Ionization Constants of 1-, 2-, and 4-Azafluorenes, Their Methyl and/or Nitro Derivatives

Compound	mp, °C	Number of determinations	pK_{min}	pK_{max}	pK_{av}
1	79-80	7	4.69	4.71	4.70
2	86-87	7	6.90	7.04	6.98
3	96.0-98.5	6	7.24	7.30	7.28
4	153-154	6	7.32	7.39	7.37
5	104-105	7	7.44	7.49	7.46
6	179.0-187.5	4	4.43	4.52	4.50
7	182-188	5	5.89	5.96	5.92
8	182-185	6	3.01	3.13	3.07
9	94-95	6	4.80	5.09	4.9
10	98-100	7	5.50	5.58	5.52
11	79-80	7	5.00	5.18	5.1
12	69-71	7	4.88	4.95	4.92

TABLE 2. Ionization Constants of 1-, 2-, and 4-Azafluoren-9-ones, Their Methyl and Carbethoxy Derivatives

Compound	mp, °C	Number of determinations	pK_{min}	pK_{max}	pK_{av}
13	127-128	7	1.46	1.52	1.50
14	142	8	4.37	4.41	4.40
15	156-157	8	5.09	5.16	5.13
16	163-168	7	4.61	4.67	4.63
17	137-138	7	1.92	2.05	1.98
18	129.0-130.5	7	2.61	2.71	2.66
19	157-158	15	2.11	2.53	2.30
20	100-103	5	2.13	2.55	2.20
21	125.5-126.0	6	0.90	1.01	0.97

All compounds **1-21** were obtained previously in our laboratory. Samples of compounds **1**, **7**, and **13** [11] were kindly provided by Professor A. T. Soldatenkov, compounds **2-6**, **9-12**, and **14-20** were obtained by the method of [7], and compounds **8** and **21** were synthesized by the procedure of [12].

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