

9-ALKYLIDENEAZAFLUORENES

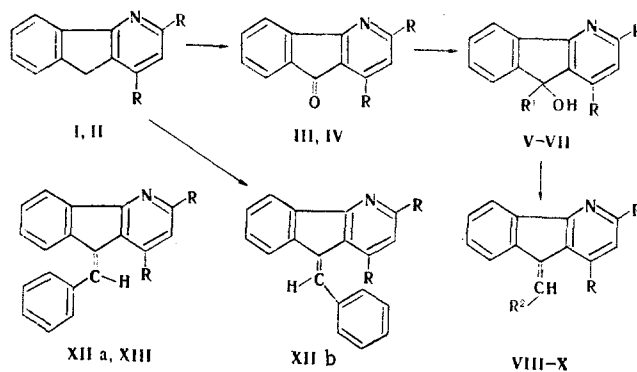
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A number of tertiary aza-9-fluorenols were obtained from 4- and 2-azafluorenones and were subjected to dehydration in order to synthesize the previously unknown 9-methyleneazafluorenes. The corresponding 9-methyleneazafluorenes and their polymers were obtained simultaneously in relatively stable form from both pyridine-ring-substituted and -unsubstituted 4-aza-9-fluorenols and from 1,3-diphenyl-2-aza-9-fluorenol. On the basis of an analysis of the mass spectrum of the polymer obtained from 9-methylene-4-azafluorene it was concluded that it is evidently isolated in the form of two dimers -- dispiro[bis(4-aza-9-fluorene)-1,3-cyclobutane] and the analogous product of dispiro addition with a 1,2-substituted cyclobutane ring. Condensation of the corresponding azafluorenes with benzaldehyde gave their 9-benzylidene derivatives in the form of geometrical isomers, the structures of which were established on the basis of the PMR spectra.

9-Methylenefluorene has not yet been isolated in attempts to synthesize it by various methods. Like fulvene, it is unstable and is rapidly converted to a polymer, to which various structures have been assigned [1-3]. The analogous azafluorene derivatives are still unknown. It therefore seemed of interest to obtain information on the possibility of their synthesis, their stabilities as a function of the position of the nitrogen atoms and substituents in the azafluorene system, and the possibility of their existence in the form of configuration isomers. Alkylidene derivatives of azafluorenes may be of interest as monomers analogous to vinylpyridines. Some compounds of this type display considerable bactericidal activity.

To obtain the 9-alkylideneazafluorenes we used 4- and 2-azafluorenes, the method for the synthesis of which is described in [4, 5]. Tertiary alcohols V-VII, which were subjected to dehydration with phosphorus pentoxide in refluxing xylene, were obtained from 4-azafluorenone (III) and from 1,3-diphenyl-4-azafluorenone (IV) and the appropriate Grignard reagents.



I, III, XII R=H; II, IV, XIII R=C₆H₅; V R=H, R¹=CH₃; VI R=C₆H₅, R¹=CH₃;
VII R=C₆H₅, R¹=C₆H₅; VIII R=R²=H; IX R=C₆H₅, R²=H; X R=C₆H₅, R²=CH₃

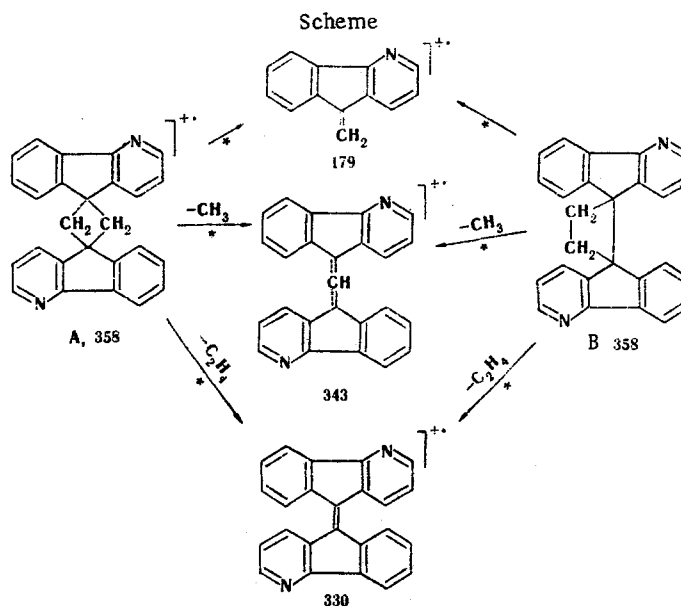
9-Methylene-4-azafluorene (VIII), which was isolated in the form of crystals with mp 42-43°C, and its dimer, which was isolated as crystals with mp 203-204°C, were obtained from alcohol V in approximately equal amounts in an overall yield of more than 10%. The mass of

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TABLE 1. Mass Spectrum of the Dimer of VIII

m/e values (relative intensities of the ion peaks in percent relative to the maximum peak)						
360 (4.8),	359 (21),	358 (69),	357 (19),	356 (17),	355 (21),	354 (6.2),
353 (8.3),	352 (10.0),	344 (3.3),	343 (5.4),	342 (6.7),	341 (7.5),	340 (3.3),
331 (4.2),	330 (14.0),	329 (40.0),	328 (9.2),	327 (7.1),	326 (4.2),	325 (4.0),
324 (6.2),	323 (3.1),	304 (2.5),	303 (6.3),	302 (5.0),	301 (7.5),	300 (4.2),
299 (4.1),	276 (3.1),	275 (6.2),	274 (3.3),	273 (3.5),	239 (4.2),	225 (4.2),
220 (2.4),	219 (7.5),	218 (3.8),	217 (3.7),	197 (6.2),	196 (12.0),	195 (9.2),
194 (9.0),	193 (9.6),	181 (6.0),	180 (20.0),	179 (100.0),	178 (13.0),	177 (6.0),
169 (9.6),	168 (4.2),	167 (7.1),	166 (4.0),	165 (9.6),	164 (4.2),	163 (4.0),
156 (5.4),	155 (14.0),	154 (5.4),	153 (5.6),	152 (5.4),	151 (8.8),	150 (5.0),
149 (17.0),	142 (6.7),	141 (25.0),	119 (15.0),	113 (7.5),	112 (5.0),	111 (10.0),
109 (7.5),	107 (6.3),	105 (10.0),	99 (12.0),	98 (8.4),	97 (14.0),	96 (7.1),
95 (12.0),	93 (5.8),	91 (7.1),	86 (3.2),	85 (24.0),	84 (9.2),	83 (20.0),
82 (7.5),	81 (17.0),	77 (8.3),	73 (8.3),	72 (3.3),	71 (34.0),	70 (10.0),
69 (27.0),	68 (6.3),	67 (10.0)				

the molecular ion with m/e 358* in the mass spectrum of the dimer (Table 1) corresponds to its empirical formula. The ion at 179 (which gives the peak with the maximum intensity) and the rearranged fragments at 343 and 330, which correspond to splitting out CH_3 and C_2H_4 groups from the molecular ions, are characteristic ions. The formation of these ions can be explained from the presence in the dimer of both the symmetrically (A) (dispiro[bis(4-aza-9-fluorene)-1,3-cyclobutane]) and unsymmetrically (B) (1,2-) substituted cyclobutane ring (see the diagram below). The possibility that the isolated dimer is a mixture of these compounds is not excluded.



Only the dimer was isolated in the case of prolonged heating of alcohol V with phosphorus pentoxide. The same dimer is formed when VIII is heated to 200°C . 1,3-Diphenyl-9-methylene-4-azafluorene (IX), which is a stable crystalline substance (mp $141-142^\circ\text{C}$), as well as its dimer (in greater than 10% yield), to which the dispiro[bis(1,3-diphenyl-4-aza-9-fluorene)-1,2-cyclobutane] (XI) structure can be assigned on the basis of mass-spectral data and the results of analysis of Dreiding models, was obtained in greater than 40% yield by dehydration of alcohol VI. The mass spectrum of dimer XI contains a molecular ion peak at 662 (98%). The ion at 331 (100%) and the rearranged fragments at 647 and 634, which are formed as a result of splitting out of CH_3 and C_2H_4 groups, confirm the presence of a cyclobutane ring.

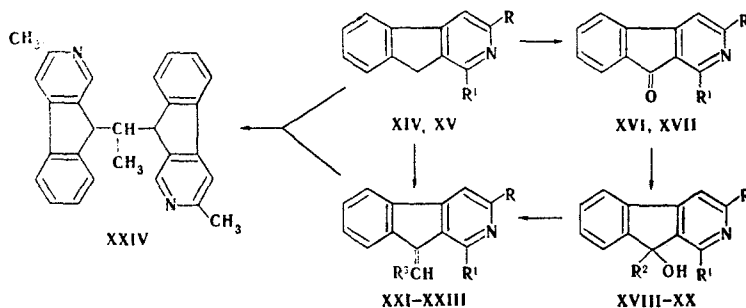
Ethylidene derivative X, which was obtained by dehydration of alcohol VII, was isolated only in the form of one geometrical isomer. A mixture of isomeric 9-benzylidene-4-azafluorenes (XII) is formed in the condensation of 4-azafluorene (I) with benzaldehyde in the presence of potassium ethoxide; workup of the mixture yielded the cis (XIIa, mp $96-98^\circ\text{C}$) and trans (XIIb, mp $62-63^\circ\text{C}$) isomers, which are formed in a ratio of 1:4. Information on their

*Here and subsequently, the numbers that characterize the ions are the ratios of the mass to the charge.

configurations was obtained from the PMR spectrum. The signals of the 1-H and 2-H protons in the spectrum of isomer XIIa are found at 7.70 and 6.94 ppm, whereas these signals are found at 7.55 and 6.75 ppm, respectively, in the spectrum of isomer XIIb. The shift of the signals to strong field in the spectrum of XIIb is due to the shielding effect of the phenyl group of the benzylidene grouping.

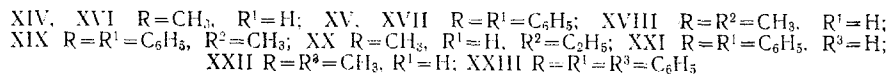
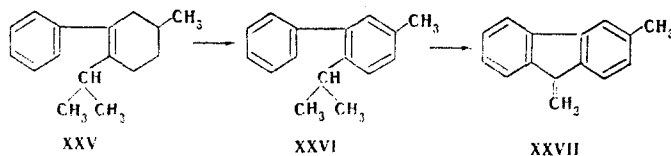
Only one isomer of 1,3-diphenyl-9-benzylidene-4-azafluorene (XIII), which, taking into account the steric factors, should have a cis configuration, was obtained in the analogous condensation of azafluorene II with benzaldehyde.

We used 3-methyl-2-azafluorenone (XVI) and 1,3-diphenyl-2-azafluorenone (XVII) as representatives of the second azafluorene system. These ketones yielded tertiary alcohols XVIII-XX, which were subjected to dehydration under the same conditions as in the preparation of azafluorenols V-VII.



We were unable to obtain 3-methyl-9-methylene-2-azafluorene by dehydration of 3,9-dimethyl-2-aza-9-fluorenol (XVIII) by means of P_2O_5 , Al_2O_3 , $KHSO_4$, $SOCl_2$, or H_2SO_4 - resinous substances are formed in all cases. The change in the position of the nitrogen atom in the azafluorene system (as compared with methylene derivative VIII) is evidently one of the reasons for the instability of this compound. However, the dehydration of diphenyl-substituted azafluorenol XIX yielded 1,3-diphenyl-9-methylene-2-azafluorene (XXI) in the form of crystals with mp 143-144°C, which did not undergo any changes on storage in a vacuum desiccator. Methylene derivative XXI undergoes quantitative conversion to azafluorenone XVII when it is oxidized.

The dehydration of azafluorenol XX gave 3-methyl-9-ethylidene-2-azafluorene (XXII), which, according to the PMR spectral data, is a mixture of geometrical isomers (in a ratio of 1:1). Both isomers of XXII (with mp 94-96 and 130-132°C) were isolated by means of chromatography. Taking into account their PMR spectral characteristics, we assigned trans and cis configurations, respectively, to them in analogy with the isomers of XII. 1,1-Bis(3-methyl-2-aza-9-fluorenyl)methane (XXIV) is formed by condensation of ethylidene derivative XXII with 3-methyl-2-azafluorene (XIV) under the conditions of the Michael reaction. Only one isomer of 1,3-diphenyl-9-benzylidene-2-azafluorene (XXIII) is formed in the condensation of azafluorene XV with benzaldehyde.



For a comparison of the stabilities of 9-methylene derivatives of 4- and 2-azafluorenes with the analogous derivatives of fluorene we undertook the synthesis of 3-methyl-9-methylenefluorene (XXVII). For this we used the method employed in the synthesis of azafluorenes I, II, XIV, and XV from the corresponding pyridine bases [4, 5]. 5-Methyl-2-isopropylidiphenyl (XXVI), which is formed in the dehydrogenation of 5-methyl-2-isopropyl-1-phenylcyclohexene (XXV) on K-16 catalyst at 400°C, undergoes dehydrocyclization on the same catalyst at 500°C; the dehydrocyclization is accompanied by splitting out of methane and, apparently, the formation of methylene derivative XXVII, which we were unable to isolate. However, the dinitrophenylhydrazone and the oxime of 3-methylfluorenone were obtained from the products of oxidation of the catalyzate.

TABLE 2. Aza-9-fluorenols

Com- pound	mp, °C (from heptane)	R _f (ether)	IR spectrum, ν _{OH} , cm ⁻¹	PMR spectrum (in CDCl ₃), δ, ppm	UV spectrum, λ _{max} (log ε), nm	Found, %			Calc., %			Yield, %
						C	H	N	C	H	N	
V	157-158	0.43	3200	7.83 (1H, q, H-3), 7.60 (1H, q, H-1), 6.80 (1H, q, H-2), 4.43 (1H, s, OH), 1.57 (3H, s, CH ₃)	212 (5.12), 284 (4.7), 310 (4.84)	79.4	5.8	6.8	79.2	5.8	7.1	90
VI	222.5-224	0.36	3322			85.8	5.5	3.9	86.0	5.4	4.0	51
VII	175-176	0.35	3318	3.6 (1H, s, OH), 2.8 (2H, q, CH ₂), 0.1 (3H, t, CH ₃)		86.0	6.1	3.9	86.0	5.8	3.9	63
XVIII	169-170	0.24		7.61 (1H, s, H-1), 2.30 (3H, s, CH ₃ -3), 1.49 (3H, s, CH ₃ -9)		79.7	6.5	6.8	79.6	6.6	6.6	62
XIX	108-110	0.37	3270	1.31 (3H, s, CH ₃ -9), 2.19 (1H, s, OH), 7.70 (1H, s, H-9)	208 (4.64), 260 (4.6), 314 (3.63)	86.0	5.6	4.0	86.0	5.4	4.0	69
XX	187-188	0.44	3220	8.05 (1H, s, H-1), 3.84 (1H, s, OH), 2.19 (3H, s, CH ₃ -3), 1.96 (2H, q, CH ₂), 0.48 (3H, t, CH ₃)	212 (5.02), 280 (4.78), 308 (4.32)	80.0	6.4	6.0	80.0	6.7	6.2	18

A white amorphous substance, which is apparently the polymer of XXVII, precipitates gradually from the catalyzate obtained in the step involving dehydrocyclization of substituted diphenyl XXVI. This precipitate decomposes above 250°C, is not soluble in any solvents, and remains unchanged on prolonged heating with potassium permanganate. In addition to an intense peak of fragment at 192 (100%), which corresponds to the molecular ion of monomer XXVII, less intense peaks of fragments appear in the higher-mass region (up to 600 amu); this confirms the polymeric character of the compound obtained.

A study of the previously unknown 9-methyleneazafluorenes described in this paper shows that they are readily polymerized. However, in contrast to 9-methylfluorene, which cannot be isolated because of its rapid conversion to a polymer, the analogous pyridine-ring-substituted and -unsubstituted 4-azafluorenes, as well as 1,3-diphenyl-9-methylene-2-azafluorene, are more stable and can be isolated. The stabilities of 9-methyleneazafluorenes depend on the position of the nitrogen atom in the pyridine ring. Methylene-group-substituted 9-methyleneazafluorenes are stable substances and, as expected, are obtained in the form of two geometrical isomers.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of the compounds were obtained with a Tesla BS-487C spectrometer with hexamethyldisiloxane as the internal standard. The UV spectra of ethanol solutions of the compounds were recorded with a Hitachi EPS-3T spectrophotometer. The mass spectra were measured with an MKh-1303 mass spectrometer. Chromatography was carried out on activity II aluminum oxide.

The characteristics of azafluorenols V-VII and XVIII-XX, synthesized from ketones III, IV and XVI, XVII, are presented in Table 2.

Dehydration of 9-Methyl-4-aza-9-fluorenol. A mixture of 2 g (0.01 mole) of alcohol V, 10 g (0.07 mole) of phosphorus pentoxide, and 80 ml of m-xylene was refluxed for 8 h, after which 70 ml of water and 150 ml of 25% ammonium hydroxide were added, and the xylene solution was separated, dried with magnesium sulfate, and worked up to give 1.2 g of a solid residue, which was chromatographed (elution with heptane) to give 0.12 g (6.6%) of methylene derivative VIII with mp 42-43°C (from hexane) and R_f 0.83 (ether). PMR spectrum (in $CDCl_3$), δ : 8.43 (1H, q, 3-H), 7.0 (1H, q, 2-H), and 5.91 ppm (1H, s, 10-H). Found: N 7.7%; M 179. $C_{13}H_9N$. Calculated: N 7.7%. Subsequent elution gave 0.1 g (5.5%) of the dimer of VIII with mp 203-204°C (from heptane) and R_f 0.54 (ether). UV spectrum, λ_{max} (log ϵ): 206 (4.5), 256 (4.0), 312 nm (4.3). Found: C 87.5; H 5.4; N 7.2%; M 358. $C_{26}H_{18}N_2$. Calculated: C 87.2; H 5.0; N 7.8%. At the end of the chromatographic process, 0.4 g (20%) of starting alcohol V was isolated.

Only the dimer of VIII was isolated in 23% yield when the same amounts of the starting reagents were heated for 12 h. A dimer with mp 203-204°C and R_f 0.54 (ether) was obtained after cooling.

Dehydration of 9-Methyl-1,3-diphenyl-4-aza-9-fluorenol. A 0.6 g (1.7 mmole) sample of alcohol VI and 3 g (21 mmole) of phosphorus pentoxide were used in the reaction. The mixture was heated for 14 h and worked up as in the preceding experiment. Chromatography [elution with heptane-ether (5:1)] gave 0.24 g (42%) of methylene derivative IX with mp 141-142°C (from heptane) and R_f 0.61 [heptane-ether (2:1)]. PMR spectrum (in $CDCl_3$), δ : 6.04 (1H, s, 10-H) and 5.58 ppm (1H, s, 10-H). Found: C 90.2; H 5.4; N 4.4%; M 331. $C_{25}H_{17}N$. Calculated: C 90.6; H 5.2; N 4.2%. Subsequent elution with heptane-ether (2:1) yielded 0.06 g (10.5%) of dimer XI with mp 293-294°C (from heptane) and R_f 0.46 [heptane-ether (2:1)]. Found: C 90.4; H 5.3; N 4.5%; M 662. $C_{50}H_{36}N_2$. Calculated: C 90.6; H 5.2; N 4.2%.

1,3-Diphenyl-9-ethylidene-4-azafluorene (X). A mixture of 0.49 g (1.35 mmole) of alcohol VII, 1 g (37 mmole) of phosphorus pentoxide, and 30 ml of m-xylene was refluxed for 8 h. After treatment with water and sodium carbonate, 0.32 g (68%) of ethylidene derivative X, with mp 152-153°C (from heptane) and R_f 0.70 [ethyl acetate-hexane (1:3)], was isolated. PMR spectrum (in $CDCl_3$), δ : 6.15 (1H, q, 10-H) and 2.06 ppm (3H, d, CH_3). Found: C 90.3; H 5.7; N 4.1%. $C_{26}H_{19}N$. Calculated: C 90.4; H 5.5; N 4.1%.

9-Benzylidene- and 1,3-Diphenyl-9-benzylidene-4-azafluorenes (XII, XIII). A 2.1 g (0.05 g-atom) sample of potassium was dissolved in 30 ml of ethanol, and a solution of 3 g (0.018

mole) of azafluorene I in 150 ml of alcohol was added. The mixture was then heated to 60°C, 3 g (0.028 mole) of benzaldehyde was added with stirring, and the mixture was refluxed for 3 h. Water (50 ml) was added, and the resulting resinous mass was chromatographed [elution with ethyl acetate—heptane (1:2)] to give 1.6 g (35%) of trans isomer XIIb with mp 62–63°C (from heptane) and R_f 0.43 [ethyl acetate—hexane (1:2)]. PMR spectrum (in CCl_4), δ : 8.21 (1H, d, 3-H), 7.85 (1H, d, 5-H), 7.55 (1H, q, 1-H), and 6.75 ppm (1H, q, 2-H). Found: C 89.2; H 5.0; N 5.4%. $C_{19}H_{13}N$. Calculated: C 89.4; H 5.1; N 5.5%. Subsequent elution gave 0.4 g (8.7%) of cis isomer XIIa with mp 96–98°C (from heptane) and R_f 0.4. PMR spectrum (in CCl_4), δ : 8.25 (1H, q, 3-H), 7.85 (1H, d, 5-H), 7.70 (1H, q, 1-H), and 6.94 ppm (1H, q, 2-H). Found: C 89.1; H 5.0; N 5.7%. $C_{19}H_{13}N$. Calculated: C 89.4; H 5.1; N 5.5%.

Benzylidene derivative XIII was similarly obtained in 92% yield from azafluorene II and benzaldehyde as orange crystals with mp 190–191°C (from alcohol) and R_f 0.70 [ethyl acetate—hexane (1:4)]. Found: C 91.1; H 5.4; N 3.5%; M 407. $C_{31}H_{21}N$. Calculated: C 91.4; H 5.2; N 3.4%.

1,3-Diphenyl-9-methylene-2-azafluorene (XXI). A mixture of 1 g (6.7 mmole) of alcohol XIX, 5 g (35 mmole) of phosphorus pentoxide, and 75 ml of m-xylene was refluxed for 9 h, after which the xylene was removed by distillation, and the residue was treated with 50 ml of water and 100 ml of 25% ammonium hydroxide and extracted with ether. Workup of the ether extract gave 0.82 g of an oily substance, from which 0.2 g (21%) of methylene derivative XXI, with mp 143–144°C (from heptane) and R_f 0.74 (ether), was isolated by chromatography [hexane—ethyl acetate (10:1)]. PMR spectrum (in $CDCl_3$), δ : 5.66 (1H, s, 10-H) and 5.97 ppm (1H, s, 10-H). UV spectrum (in alcohol), λ_{max} (log ϵ): 205 (4.82), 260 (4.80), 328 (4.20). 396 nm (2.50). Found: C 90.3; H 5.3; N 4.5%; M 331. $C_{25}H_{17}N$. Calculated: C 90.6; H 5.2; N 4.2%. Oxidation of XXI (with $KMnO_4$ in acetone at 60°C) gave azafluorenone XVII (mp 182–183°C) in 93% yield.

3-Methyl-9-ethylidene-2-azafluorene (XXII). Dehydration of 0.3 g (3 mmole) of alcohol XX (with 1 g of P_2O_5 in 20 ml of m-xylene after 15 h) gave 0.18 g (64%) of a mixture of isomers of ethylidene derivative XXII. PMR spectrum (in CCl_4), δ : 8.70 (0.5H, s, 1-H), 8.48 (0.5H, s, 1-H), 2.45 (3H, s, 3- CH_3), 2.30 (1.5H, d, 10- CH_3 , $J = 7$ Hz), and 2.23 ppm (1.5H, d, 10- CH_3 , $J = 7$ Hz). Found: N 6.6%. $C_{15}H_{13}N$. Calculated: N 6.8%.

Chromatography of the mixture [ethyl acetate—heptane (1:2)] yielded 0.024 g (13%) of the trans isomer with mp 94–96°C (from heptane) and R_f 0.66 (ether). Found: N 6.7%, M 207. $C_{15}H_{13}N$. Calculated: N 6.8%. Subsequent elution gave 0.01 g (5.5%) of the cis isomer with mp 130–132°C (from heptane) and R_f 0.61. Found: N 6.7%; M 207. $C_{15}H_{13}N$. Calculated: N 6.8%.

1,3-Diphenyl-9-benzylidene-2-azafluorene (XXIII). A mixture of 1 g (3.1 mmole) of azafluorene XV, 1.05 g (9.9 mmole) of benzaldehyde, and 10 ml of a 10% solution of potassium ethoxide was refluxed for 6 h, after which the alcohol was removed by distillation, and the residue was crystallized from heptane to give 0.3 g (23%) of benzylidene derivative XXIII as orange crystals with mp 193–195°C (from heptane) and R_f 0.71 [ethyl acetate—hexane (1:4)]. Found: C 91.3; H 5.1; N 3.5%; M 407. $C_{31}H_{21}N$. Calculated: C 91.4; H 5.2; N 3.4%.

1,1-Bis(3-methyl-2-aza-9-fluorenyl)methane (XXIV). A mixture of 0.25 g (1.4 mmole) of ethylidene derivative XXII, 0.5 g (2.8 mmole) of azafluorene XIV, 5 ml of pyridine, and 0.25 ml of a saturated solution of potassium hydroxide was heated at 100°C for 1.5 h, after which the pyridine was removed by distillation, and the residue (0.63 g) was chromatographed to give, successively, 0.26 g (52%) of azafluorene XIV and 0.1 g (21%) of XXIV as orange crystals with mp 118–119°C (from ligroin). Found: C 86.7; H 6.2; N 7.2%; M 388. $C_{28}H_{22}N_2$. Calculated: C 86.6; H 6.2; N 7.2%.

5-Methyl-2-isopropylidiphenyl (XXVI). This experiment was carried out in a flow system with a quartz contact tube and K-16 catalyst (17 ml). The temperature in the catalyst zone was 395–400°C. A solution of 4.7 g of substituted cyclohexene XXV in 10 ml of benzene was passed at a constant rate through the contact tube in the course of 40 min. A total of 1 liter of gas was collected (at 748 mm and 23°C; H_2 97%, C_7H_{12} 1.8%, $C_7H_{12}+2$ 0.7%, and CO_2 5%). Distillation of the catalyzate gave 1.6 g (34.8%) of XXVI with bp 114–117°C (3 mm), n_D^{20} 1.5535, and d_4^{20} 0.9669 [6]. Found: C 91.6; H 8.1%; M 210; MR_D 69.5. $C_{16}H_{18}$. Calculated: C 91.4; H 8.5%; MR_D 68.9.

Dehydrocyclization of 5-Methyl-2-isopropylidiphenyl. The reaction was carried out on the same catalyst (50 ml) at 490–500°C. A solution of 15 g of XXVI in 40 ml of benzene was

passed through the contact tube in the course of 2.5 h. A total of 3.1 liters of gas was collected (at 757 mm and 28°C; H₂ 81%, CH₄ 16.9%, C₂H₂n 1.66%, and CO₂ 0.43%). A total of 0.12 g of a polymer gradually precipitated as a white amorphous substance from the residue after distillation from the catalyzate of the benzene and 8.5 g of starting XXVI. The polymer decomposed at 256°C.

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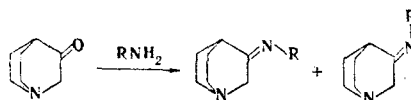
THREE-DIMENSIONAL STRUCTURE OF 3-IMINOQUINUCLIDINES

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The syn-anti isomerism of some 3-iminoquinuclidines was studied by means of ¹H and ¹³C NMR spectroscopy with a paramagnetic-shift reagent [Eu(DPM)₃]. The conformations and configurations of these compounds were established, and the differences in the free energies of the isomers and the free energies of activation of the isomerization were calculated.

In connection with the search for antihistamine preparations among quinuclidine derivatives we synthesized 3-iminoquinuclidines by reaction of 3-quinuclidone with alkyl-, aryl-, and heteroarylamines in toluene or xylene in the presence of p-toluenesulfonic acid with removal of the water by azeotropic distillation.



I R = C₆H₄CH₃-*m*; II R = C₆H₄CH₃-*p*; III R = C₆H₄Cl-*o*; IV R = C₆H₄Cl-*p*;
V R = C₆H₄COOC₂H₅-*p*; VI R = (C₅H₄N)- α ; VII R = (α' -CH₃C₅H₃N)- α ; VIII R = (C₅H₄N)- β ;
IX R = CH₂C₆H₅; X R = CH₂CH₂OH; XI R = CH₂CH₃

Since the 3-iminoquinuclidine molecules contain an exocyclic C=N bond, one might have assumed that these compounds would exist in the form of syn and anti isomers. The present paper is devoted to the study of this isomerism and the conformations of the indicated compounds by NMR spectroscopy.

Two sets of signals — multiplets of the β protons of the quinuclidine ring at 1.7-1.9 ppm, quintets of the γ protons at 2.4-2.7 ppm, multiplets of the α protons at 2.7-3.0 ppm, and singlets of the α' protons (attached to the 2-C atom of the quinuclidine ring) at 3.0-3.6 ppm, and a multiplet of the protons of the aryl substituents at 6.5-7.5 ppm (Fig. 1a and Table 1) — are observed in the ¹H NMR spectra of I-XI recorded at room temperature. This confirms the assumption of the existence of the investigated compounds in the form of a mixture of syn and anti isomers that undergo interconversion relatively slowly. Depending on the substituents, the isomer ratio ranges from 1.2:1 to 5:1. (See scheme on following page.)

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