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1-(FLUOREN-2-YL)-2-(2-AZAFLUOREN-3-YL)ETHENE AND 1-(FLUOREN-2-YL)-2-(2H,2-METHYLINDENO[2,3-c]PYRIDINE)ETHENE

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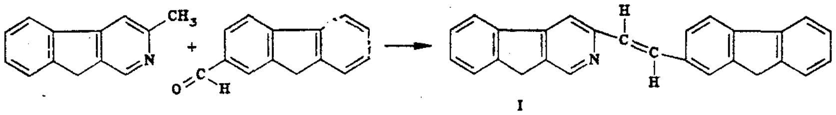
UDC 547.678.3'828:541.65

Condensation of 3-methyl-2-azafluorene with 2-formylfluorene results in the formation of a compound containing a polyconjugated system and two acidic CH centers, namely, 1-(fluoren-2-yl)-2-(2-azafluoren-3-yl)ethene. The conversions of this compound upon treatment with alkali have heen studied by electronic absorption spectroscopy. The methyl iodide derivative of this base was used as an intermediate in the preparation of a pseudo-azulene, 1-(fluoren-2-yl)-2-(2H, 2-methylindeno[2,3-c]pyridine)ethene.

In order to prepare polyconjugated systems containing fluorene and azafluorene fragments, and to study their optical properties, we have carried out the condensation of 3-methyl-2-azafluorene [1] with 2-formylfluorene. 1-(Fluoren-2-yl)-2-(2-azafluoren-3-yl)ethene (I) was obtained in 30% yield and isolated chromatographically in pure form as light yellow crystals, mp 190-192°C. The IR spectrum of compound (I) exhibited the C=C stretching vibration and out-of-plane deformation bands at 1675 and 965 cm^{-1}, respectively, which confirms the trans-configuration about the double bond. In the electronic absorption spectrum of compound (I) (Fig. 1a), the long-wavelength band at λ_{max} 346 nm (log ε 4.42) is shifted bathochromically by 46 nm relative to the corresponding band in 3-methyl-2-azafluorene (Fig. 2, 1), which may be explained in terms of an increase in the degree of conjugation in compound (I).



I

Compound (I) is a di-CH-acid (active methylene groups of the fluorenyl and azafluorenyl fragments), and we thus investigated the conversions of this compound upon treatment with

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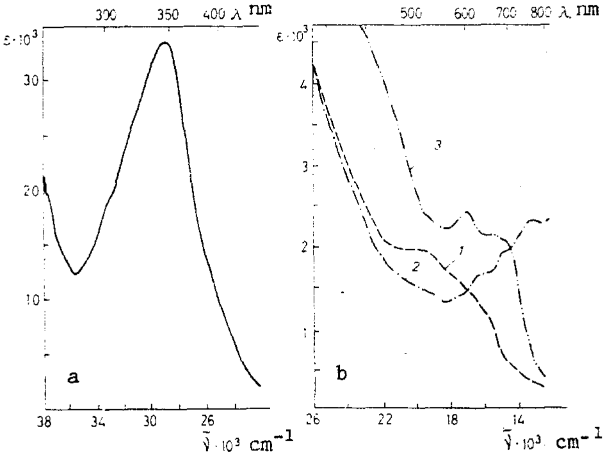


Fig. 1. Experimental electronic absorption spectra: a, compound (I) in DMSO; b, 1, carbanion A (compound (I) in DMSO + KOH; red solution); 2, dicarbanion B (compound (I) in DMSO + KOH after 30 min; dark blue solution); 3, compound (III) in 96% alcohol.

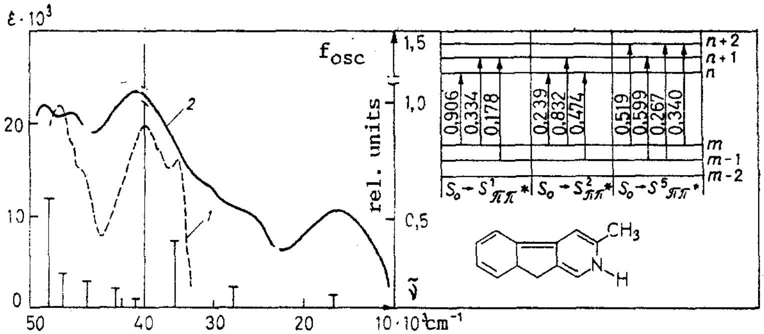
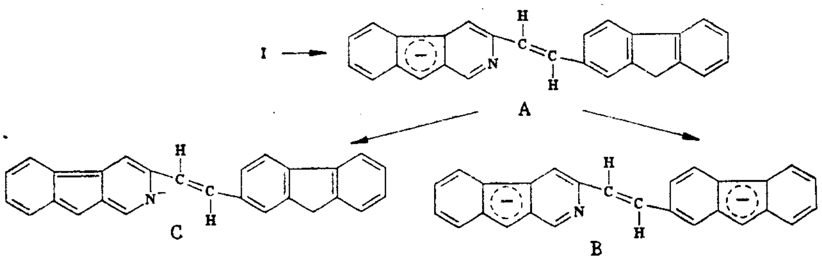


Fig. 2. Experimental electronic absorption spectra: 1) 3-methyl-2-azafluorene (in alcohol); 2) carbanion of 3-methyl-2-azafluorene, prepared by basification of an ethanol solution of the methyl iodide of 3-methylazafluorene (C_2H_5OH + KOH). Frequencies ($\tilde{\nu}$) and oscillator strengths (f_{osc}) of electronic transitions, and the contributions of the main configurations to the $S^1_{\pi\pi}*$, $S^2_{\pi\pi}*$, and $S^5_{\pi\pi}*$ excited states, were calculated by CNDO with CI for the carbanion of 3-methyl-2-azafluorene (using a pseudo-azulene structural approximation).

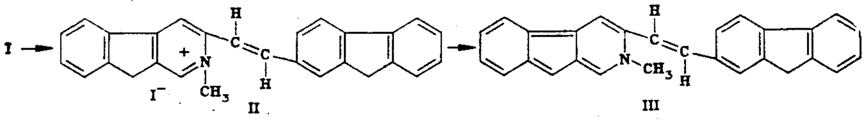
alkali. This was accomplished by recording its electronic spectra in DMSO solutions in the presence of crystalline KOH.

Addition of alkali to a light yellow solution of (I) results in an immediate color change to red. New absorption bands appear in the electronic spectrum at λ_{max} 520 nm (log ε 4.35) and 598 nm (log ε 3.18) [Fig. 1b (1)]; these bands are characteristic of the carbanion of 3-methyl-2-azafluorene. The experimental spectrum is compared in Fig. 2 with its spectrum calculated by PPO with CI using a modified program for the variable β approximation [2-4], which gave values of λ_{max} for the $S_0 \rightarrow S^1_{\pi\pi}*$ electronic transitions and the associated oscillator strengths. The lowest energy $S_0 \rightarrow S^1_{\pi\pi}*$ transition is from the highest occupied molecular orbital to the lowest unoccupied molecular orbital and is located at λ_{max} 601 nm and of low intensity, which is qualitatively consistent with the experimental spectrum. Thus, compound (I) undergoes deprotonation first at the azafluorene fragment to give carbanion A. However, the red color of the solution is maintained only a short period of time in the presence of oxygenated atmosphere (5-10 min). The solution gradually darkens, and after 30 min the solution exhibits a stable dark blue color. The electronic absorption spectrum in the visible range (for the dark blue solution) has bands at λ_{max} (log ε): 350 (4.58), 500 (3.23), 598 (3.18), 630 (3.29), 675 (3.33), and 750 nm (3.40) [Fig. 1b (2)].

Anion A can be converted to two possible structures: it can undergo deprotonation at the fluorenyl fragment to form dianion B, or it could be converted to the pseudo-azulene system C, which can be stabilized as an ion pair in DMSO. In fact, however, the bands in the 598-750 nm region and the dark blue color are characteristic of pseudo-azulenes [5].



The azafluorenyl fragment in compound (I) was converted to the pseudoazulene structure in the conventional manner.



Base (I) was converted to its methyl iodide (II). Treatment of a suspension of the latter in benzene with 5% aqueous KOH resulted in the formation of 1-(fluoren-2-yl)-(2H,2-methylideno[2,3-c]pyridin)ethene (III), which was separated as dark crystals, mp 179-181°C. An alcohol solution of this material was dark blue. The electronic absoprtion spectrum contains the following bands at λ_{max} (log ε): 357 (3.83), 425 (3.75), 588 (3.42), 654 (3.36), and 690 nm (3.33) [Fig. 1b (3)].

The spectral characteristics of pseudoazulene III and anion IA, formed from compound (I) in DMSO in the presence of potassium hydroxide, are very similar.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer for KBr pellets; electronic spectra in DMSO solutions were obtained on a Specord UV-Vis (at $c = 10^{-3}$-10^{-5} M). Mass spectra were taken on an MX-1303 spectrometer.

1-(Fluoren-2-yl)-2-(2-azafluoren-3-yl)ethene (I). A mixture of 0.2 g (1.1 mmole) 3-methyl-2-azafluorene and 0.23 g (1.1 mmole) of 2-formylfluorene was treated with 15 ml of acetic anhydride and heated at reflux for 16 h. Excess anhydride was removed in vacuo. The reaction product was extracted with ether and dried over magnesium sulfate. The residue (0.3 g) remaining after evaporation of the ether was chromatographed on aluminum oxide with hexane eluent. Yield, 0.12 g (30.5%), light yellow crystals, mp 190-192°C (from hexane), R_f 0.53 (ethyl acetate—hexane, 1:4, mixture). Found: C 91.1; H 5.5; N 3.6%. M^+ 357. $C_{27}H_{19}N$. Calculated: C 90.8; H 5.3; N 3.9%; M^+ 357.

Methyl Iodide of 1-(Fluoren-2-yl)-2-(azafluoren-3-yl)ethene (II). A solution of 0.8 g (2.2 mmole) of compound (I) and 3.1 g (22 mmole) of methyl iodide in 40 ml acetone was kept for 24 h. The resulting precipitate was removed by filtration and washed with acetone. Yield 0.6 g (53%), orange crystals, mp 210-212°C (dec.). Found: N 2.6%. $C_{27}H_{19}N \cdot CH_3I$. Calculated: N 2.8%.

1-(Fluoren-2-yl)-2-(2H,2-methylindeno[2,3-c]pyridine)ethene (III). A suspension of 0.25 g (0.5 mmole) of salt (II) in 15 ml benzene was stirred vigorously as 10 ml of 5% KOH was added. The organic layer was separated. The reaction products were extracted from the aqueous solution with benzene. The residue after evaporation of the benzene was washed with water until it no longer exhibited a basic reaction. Yield 0.11 g (58%), dark crystals, mp 178-181°C. Found: N 3.8%; M^+ 371. $C_{28}H_{21}N$. Calculated: N 3.8%; M^+ 371.

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SPECTRAL STUDY OF 3-HYDROXYPYRIDINE AND 8-HYDROXYQUINOLINE IN GASEOUS PHASE

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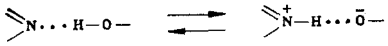
The IR spectral data of 3-hydroxypyridine and 8-hydroxyquinoline in the condensed state show that the two compounds are present in ionic form, while in the gaseous-phase state they are present in a neutral form. In 8-hydroxyquinoline in the gaseous-phase, a weaker intramolecular hydrogen bond is retained than in the CCl_4 solution.

Much attention is being paid at present to the study of compounds in the gaseous phase by physical methods [1, 2]. Both physical and chemical properties of the compounds are being studied, and by comparison with the data for the condensed state (solution, crystal), we can evaluate the influence of different types of intermolecular interactions on the electron density distribution in the molecule, its structure, conformational features, reactivity, etc.

The present article is a continuation of previously reported studies on the structural features of 9,10-anthraquinone derivatives in the gaseous phase and condensed states by the IR spectroscopy [3, 4], and is directed to the study of 3-hydroxypyridine (I) and 8-hydroxyquinoline (II). The structure of compounds I and II in the condensed state (solution, crystal) has until now been studied in a fair detail [5, 6]. However, the presence of strong intermolecular (for I) and intramolecular (for II) hydrogen bonds made it difficult to determine the positions of the proton:



A B

The available data on the structure of 8-hydroxyquinoline in the crystalline state and in solutions in protonic solvents are interpreted as corresponding to the Zwitterionic form B [5]. In the present work, results are given for the study of the structure of compounds I and II in the gaseous phase, in which the intermolecular dissociates decompose and the individual free molecules can be studied. The results obtained are shown in Table 1 and Figs. 1 and 2.

In the IR spectrum of the crystalline compound I, a very broad absorption band is observed with anomalously low frequency and with maxima at about 2500 and 1850 cm^{-1}. The spectrum of the crystalline O-deuterated derivative I is characterized by the appearance of additional bands at 2140, 1439, and 1042 cm^{-1}, so that the absorption bands of compound (I) in the 3000-1800 cm^{-1} region can be assigned to the OH (or HN^+) vibrations. All the frequency shifts during the isotopic substitution are close to theoretical: 2920/2410 = 1.33; 1880/1440 = 1.30; 1380/1042 = 1.32. On transition into a gaseous phase, the spectra of compound I and the O-deutrated derivative of I differ substantially in the absence of absorption bands

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