UNUSUAL LIGHT ABSORPTION OF gem-POLYFURYLALKANES IN SULFURIC ACID SOLUTION

Yu. M. Shapiro

The UV spectra of gem-polyfurylalkanes in concentrated sulfuric acid have intense bands that are shifted bathochromically as a function of the number of furan rings in the molecule. It was concluded that the conjugation between the rings through the formally nonconducting carbon bridge develops in an ionizing medium. An interpretation of the results is proposed.

In an investigation of the state of gem-polyfurylalkanes in concentrated sulfuric acid solutions we found that the spectra of these compounds have an intense light-absorption band that is bathochromically shifted as the number of rings (n) in the molecule increases (Fig. 1) in accordance with the empirical dependence

$$\lambda_{\max} = 1000/(5.14 - n),\ \text{nm};\ \theta_{\max} = (5.14 - n)\ .\ 10^4,\ \text{cm}^{-1}$$

Furan and α-methylfuran (sylvan) have a band with a maximum at 240 nm, difurylmethanes with various types of alkyl groups (Fig. 2) have a band in the zone 320 ± 10 nm, and trifurylmethanes have a band at 470 ± 5 nm. The extinction as a function of the number of rings. Complete or partial replacement of the hydrogen atom attached to the central carbon atom in di- or trifurylmethane does not have a substantial effect on the location and intensity of the bands (see, for example, Fig. 2, spectra 1 and 2).

This sort of shift would be natural for compounds with π conjugation between the rings; however, it does not agree with the conventional concepts for molecules of the group under consideration.

The UV spectra of alcohol solutions are virtually identical, regardless of the number of furan rings in the molecule: $\lambda_{\max}$ 222 ± 2 nm, $\log\varepsilon$ 4.3 ± 0.2. This is in agreement with the known concepts regarding the light absorption of aromatic and other compounds with an isolating carbon bridge.

Experiments with toluene and di- and triphenylmethane did not reveal anomalous phenomena in a series of gem-polyphenylalkanes. The spectra of sulfuric acid and alcohol solutions of these compounds have an intense band at ≈ 220 nm, which in time is replaced by at band at 230-240 nm, apparently as a result of the formation of sulfo derivatives.

We have previously [1] established that furan derivatives at the concentrations on the order of 10^{-5} mole/liter that are used in spectroscopy exhibit relatively high stability in sulfuric acid solutions (when certain methods for their preparation are observed). In contrast to benzene homologs, furylalkanes in this case do not undergo sulfonation, and the spectra of the substances remain unchanged at 5-20°C for more than 24 h. From solutions with a polyfurylalkane concentration of 10^{-2} mole/liter (0.2-0.4%) by ether extraction one can obtain an oil and identify it from its IR spectrum as being the starting compound. The mass undergoes resinification at higher concentrations.

To interpret the experimental data one can take into account factors that have recently been undergoing ever increasing development. Thus in [2, 3] stabilization of pentacoordinated carbon in superacid media was demonstrated by quantum-mechanical calculations on the basis of real compounds of the $CH_5{}^+An$ type. Furylalkanes have higher basicities, and their

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TABLE 1

n	λ_{max}, nm	
	exptl.	calc.
1	240	241
2	320	318
3	470	467
4	—	877
(5	—	7142)

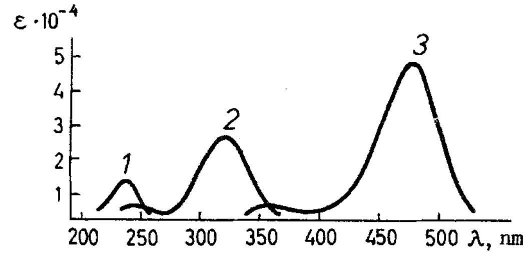
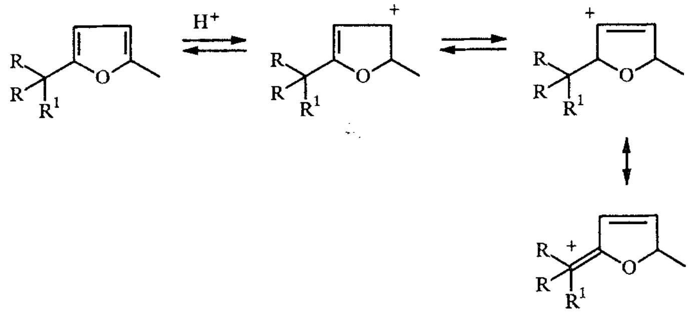


Fig. 1. Electronic spectra of furylalkanes in concentrated sulfuric acid: 1) 2-methylfuran; 2) 2,2-bis(5-methyl-2-furyl)propane; 3) 1,1,1-tris(5-methyl-2-furyl)ethane.

ionization may be realized, as follows from our spectral data, in concentrated sulfuric acid; this leads to the formation of the overall conjugated system



R, R^1 = H, alkyl, 2-furyl

Calculations by means of the experimentally found empirical dependence give λ_{max} values that are in good agreement with the experimental values and make it possible to determine the spectrum of tetra(2-furyl)methane (n = 4) and also allow for the possibility of the formation of compounds of the CR_5^+ type (n = 5) with a band in the near-IR region.

EXPERIMENTAL

The UV spectra were obtained with a VSU-2P spectrophotometer.

The polyfurylalkanes were synthesized by the methods in [4, 5].

The solutions were prepared in the following way. A weighed (≈ 1 g) sample of the substance was dissolved in glacial acetic acid in a 25-ml volumetric flask. From the first flask a 1-ml sample was also dissolved in acetic acid in a 25-ml volu-

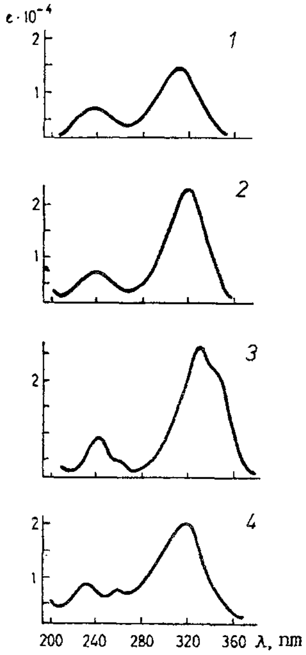


Fig. 2. Electronic spectra of gem-difurylalkanes in concentrated sulfuric acid: 1) 1,1-bis(5-methyl-2-furyl)ethane; 2) 2,2-bis(5-methyl-2-furyl)propane; 3) 1,1-bis(5-methyl-2-furyl)cyclohexane; 4) ethyl 3,3-bis(5-methyl-2-furyl)butyrate.

metric flask, after which a 0.2-ml sample was dissolved dropwise with vigorous stirring in concentrated sulfuric acid in a 100-ml volumetric flask. The resulting solution corresponded to a concentration of $(1\text{-}4)\cdot10^{-5}$ mole/liter of the furylalkane.

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