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Electronic Absorption Spectra of Arylmethylene, Ethylidene, and Allylidene 3*H*-Furan-2-one Derivatives

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Abstract—The electronic absorption spectra of 3*H*-furan-2-ones containing substituents with varied length of the conjugation chain in position C^3 of the heteroring are examined. The conclusions are made about the direction of the band shift depending on the structure and size of the conjugation system of the substituents.

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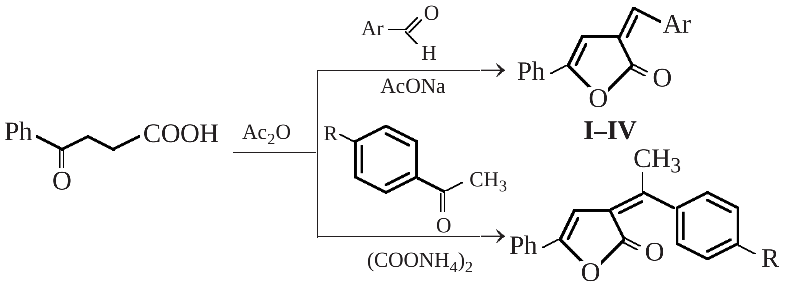
In this study we examined arylmethylene, ethylidene, and allylidene derivatives of 3*H*-furan-2-ones, which are widely used as intermediates in the synthesis of various ali- and heterocyclic compounds exhibiting the biological activity.

Electronic spectroscopy is the best experimental tool for studying conjugated systems and fine structures of organic compounds.

The presence of the conjugated C=C, C=O bonds and the aromatic ring with substituents of different nature in the 3*H*-furan-2-one derivatives that we study allows the molecule to be considered as an integrated resonator. The aim of our study was to establish the characteristic conjugated system responsible for the absorption and to correlate the nature of substituents with the absorption band shifts.

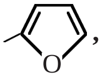
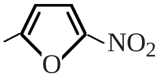
Published data concerning this problem are scarce. There are only a few articles dealing with the effect of substituent in position 5 of the heteroring [1] on the color of the compounds [2] and on the shift of the absorption bands in the UV spectra of 5-aryl-3-benzylidene-3*H*-furan-2-ones.

Arylmethylene (**I**–**V**) and ethylidene (**VI**–**VIII**) derivatives of 3*H*-furan-2-one were prepared by condensation of 4-oxo-4-arylbutanoic acids with aromatic aldehydes [3] and alkylaromatic ketones [4] according to the published procedures.



I–IV

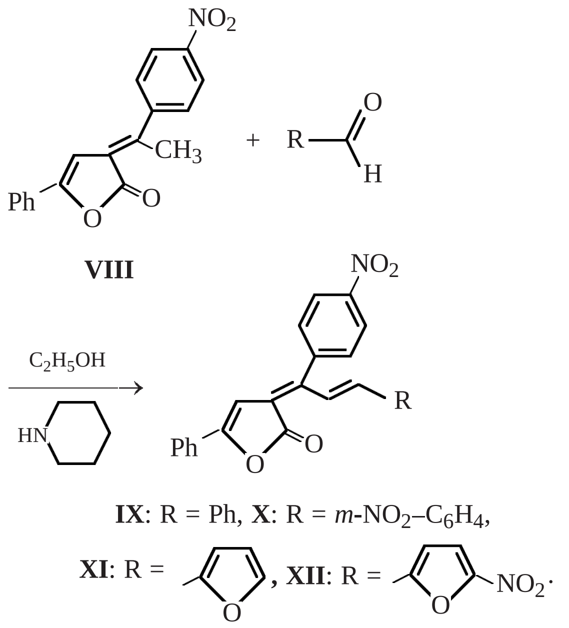
VI–VIII

I: Ar = Ph, **II**: Ar = 4-NO_2–C_6H_4, **III**: Ar = 3-NO_2–C_6H_4, **IV**: Ar = , **V**: Ar = ,

VI: R = H, **VII**: R = Cl, **VIII**: R = NO_2.

The structure of compounds **VI**–**VIII** suggests that the methyl group protons are labile, because of the effect of the carbonyl group in the furan ring, the exocyclic C=C bond, and also the activating effect of the electron-withdrawing substituent in the aromatic ring. These factors allow 3-ethylidene-3*H*-furan-2-ones **VI**–**VIII** to be used as methylene components in the condensation with aromatic aldehydes [5].

We have used the aldehydes of the aromatic and heterocyclic series.



VIII

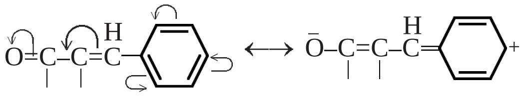
IX: R = Ph, **X**: R = *m*-NO_2–C_6H_4,

XI: R = , **XII**: R = .

According to the IR and ^1H NMR data, the compounds prepared were identified as 5-phenyl-3-[3-(R-phenyl)-1-(4-nitrophenyl)allylidene]-3*H*-furan-2-ones **IX** and **X**, and 5-phenyl-3-[3-(5-R^1-furyl)-1-(4-nitrophenyl)allylidene]-3*H*-furan-2-ones **XI** and **XII**.

The UV spectra of **I**–**XII** mainly contain two absorption bands (see table). The absorption band with λ_{max} 260 nm is common for all the 3*H*-furan-2-one derivatives and belongs to the C=C–Ph fragment. The chromophore responsible for the second absorption band with λ_{max} 361–455 nm includes the conjugated carbonyl fragment O=C–C=C–Ar. Hence, the 3*H*-furan-2-one arylidene derivatives contain active α,β-unsaturated carbonyl fragment, which accounts for their participation in the Michael condensation and the previously reported results of the reaction with Grignard reagents [6].

To account for the effect of substituents on the absorption band location, it is necessary to consider the structure of the α,β-unsaturated carbonyl fragment with the formal charge resulting from the π-electron transfer.



It can be seen from the resonance structure that the effect of polar substituents in *p*-position (–NR_2, –OR, –NO_2) will be the most significant. These substituents make longer the effective chain of the conjugated system with electron transfer, which causes the bathochromic shift of the absorption band (Fig. 1, compounds **I** and **II**).

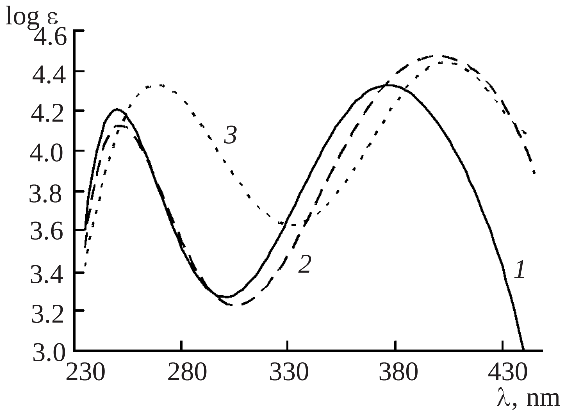
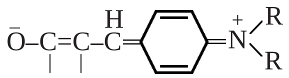
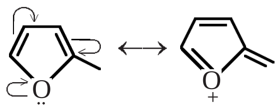


Fig. 1. Absorption band shift depending on the substituent in the C^3 position of 3*H*-furan-2-one. (*1*) **I**, (*2*) **II**, and (*3*) **IV**.



Introduction of the furyl residue instead of the phenyl group also causes a bathochromic shift (compounds **I** and **IV** in Fig. 1), which is caused by excess π-electron density in the furan ring and involvement of the lone electron pair of oxygen in the common conjugation chain.



UV spectral parameters of **I**–**XII**

Comp. no.	λ_{max1}, nm	log ε_1	λ_{max2}, nm	log ε_2
I	262	4.14	389	4.36
II	260	4.14	410	4.47
III	260	4.42	391	4.39
IV	260	4.05	409	4.26
V	260	4.13	445	4.25
VI	260	4.14	361	4.45
VII	260	4.12	373	4.42
VIII	260	4.14	375	4.45
IX	260	4.45	395	4.46
X	260	4.37	400	4.38
XI	260	4.39	415	4.39
XII	266	4.32	455	4.52

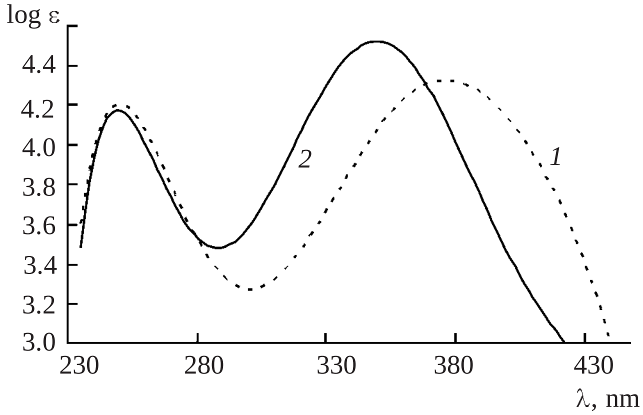


Fig. 2. Absorption band shift of 5-phenyl-3-phenylethylidene-3*H*-furan-2-one **VI** as compared to 5-phenyl-3-phenylmethylene-3*H*-furan-2-one **I**. (*1*) **I** and (*2*) **VI**.

The absorption band of 3*H*-furan-2-one ethylidene derivatives **VI**–**VIII** is shifted hypsochromically as compared to arylmethylene derivatives **I**–**V**, which is probably due to the effect of the methyl group. This group sterically hinders the existence of the planar resonance structure (Fig. 2).

It is known that the interaction in conjugated unsaturated systems is the strongest when the unsaturated groups are coplanar. If their planes form angle α, the resonance energy will be proportional to $\cos^2\alpha$ (Fig. 3).

Figure 3 shows that small angles (up to 20°C) do not noticeably distort the conjugation as compared to the planar system, whereas at large rotation angles the interaction between the unsaturated groups becomes negligible, and the chromophores become essentially separated.

Proceeding from this standpoint, we carried out quantum-chemical calculations of the geometry of arylmethylene (**I**–**V**) and ethylidene (**VI**–**VIII**) 3*H*-furan-2-one derivatives by the PM3 method using the MOPAC program (Fig. 4). These calculations showed that for 3-arylmethylene-3*H*-furan-2-one the phenyl ring deviates from the heteroring plane by 18.3°, whereas in 3-ethylidene-3*H*-furan-2-one the dihedral angle is as large as 52.1°. This fact accounts for the difference in the electronic absorption spectra.

For allylidene derivatives of 3*H*-furan-2-ones **IX**–**XII**, the absorption band is shifted bathochromically as compared to the corresponding arylmethylene derivatives **I**–**V**, which is due to the presence of an additional dimethine group and to an increase in the effective length of the conjugated system (Fig. 5).

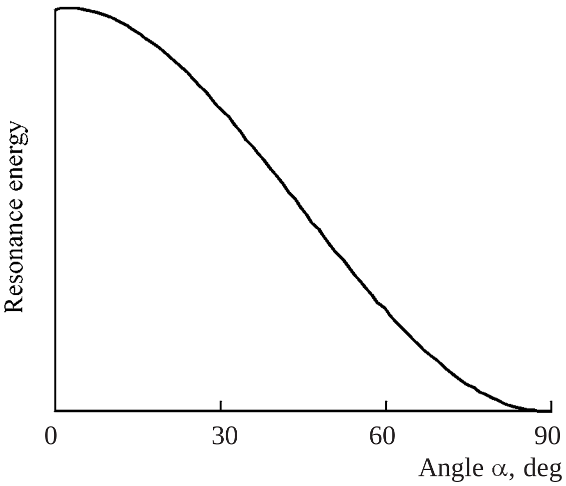
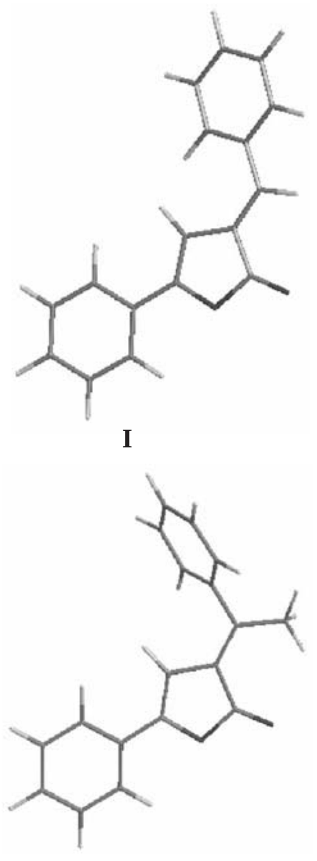


Fig. 3. Resonance energy as a function of angle α between the planes of the conjugated chromophores.



VI

Fig. 4. Steric structures of 5-phenyl-3-phenylmethylene-3*H*-furan-2-one **I** and 5-phenyl-3-phenylethylidene-3*H*-furan-2-one **VI**.

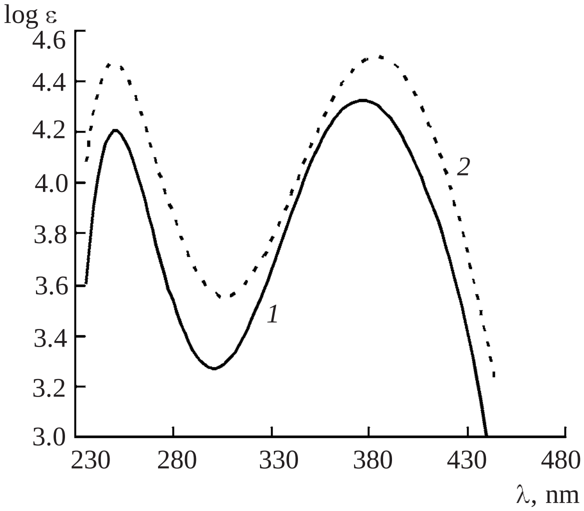


Fig. 5. Absorption band shift for 5-phenyl-3-[3-phenyl-1-(4-nitrophenyl)allylidene]-3*H*-furan-2-one **IX** as compared to 5-phenyl-3-phenylmethylene-3*H*-furan-2-one **I**. (*1*) **I** and (*2*) **IX**.

Thus, in the series of arylmethylene, ethylidene, and allylidene 3*H*-furan-2-one derivatives the absorption band at 361–415 nm belongs to the O=C–C=C–Ar enone group, and its location depends on the nature of substituents in the aromatic ring, on the steric factors, and on the size of the conjugated system.

EXPERIMENTAL

The UV spectra were taken on an SF-201 spectrophotometer from 10^{-5} M solutions of compounds in chloroform.

Arylmethylene (**I**–**V**), ethylidene (**VI**–**VIII**), and allylidene (**IX**–**XII**) 3*H*-furan-2-one derivatives were prepared by the previously described procedures [3–5].

ACKNOWLEDGMENTS

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