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BRIEF COMMUNICATIONS

ULTRAVIOLET ABSORPTION SPECTRA OF 2-SUBSTITUTED-1-(*p*-VINYLPHENYL)CYCLOPROPANES

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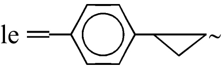
UV spectra of 2-substituted-1-(*p*-vinylphenyl)cyclopropanes are studied. Based on spectral data, different substituents (—X) are characterized with respect to their effect on the system of conjugated bonds in the molecule ~X. The cyclopropane ring is found to be a part of the conjugated system of the whole molecule.

Keywords: 2-substituted-1-(*p*-vinylphenyl)cyclopropane, UV spectrum, cyclopropane ring, conjugation, substituent.

At present, functionally substituted cyclopropanes attract close attention of many researchers because these compounds combine highly reactive and mutually affecting fragments, which can be considered as a base to synthesize polymeric compounds with a desired complex of valuable properties [1-3].

In most cases, it proves to be not enough to study the effect of different substituents attached to the benzene ring through the cyclopropane ring by various physical methods, though they help to gain diverse information on the mutual effect of substituents in complex molecules.

A series of compounds of this type has been studied by NQR [4], where based on NQR data the analogy was noticed between the corresponding derivatives of cyclopropane and ethylene. The similarity of NQR frequencies of chlorocyclopropane and chloroethylene indicates that the electronic effect of substituents identically affects the chlorine atoms through the cyclopropane ring and ethylene bond.

A coincidence in that the electronic effect of substituents is passed through the three-membered cyclopropane ring and ethylene double bond the authors explain by almost the same type of hybridization of carbon atoms of the cyclopropane ring and ethylene bond, i.e. all three carbon atoms of the ring are in the sp^2-hybridization state [5].

Other authors have stated that the saturated cyclopropane ring can conjugate with unsaturated moieties (C=C, C=O, C_6H_5) bonded to it. However, the question about a possibility to pass electronic effects through the cyclopropane ring remains open because, according to the data of PMR spectra, the π-character of the carbon-carbon bond in cyclopropane slightly manifests itself, and therefore, such a possibility is weakened and can be complicated by other effects [6].

The purpose of the work is to study the capability of the cyclopropane ring to pass the effect of groups bonded to it in 2-functionally substituted-1-(*p*-vinylphenyl)cyclopropanes by UV spectroscopy. Hence, we analyzed the UV spectra of

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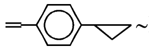
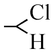
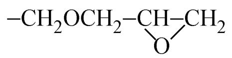
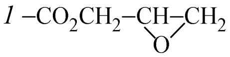
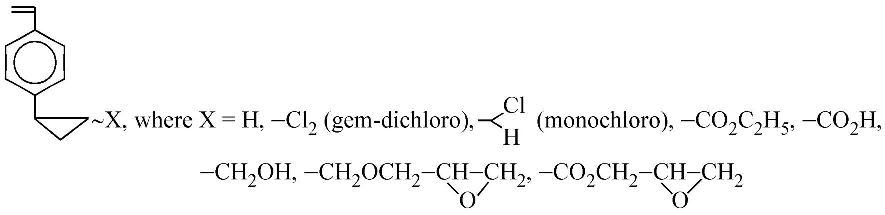
TABLE 1. Absorption Bands in the UV Spectra of the Compounds

Model compounds and the group X in  ~X	λ_1, nm (lg ε_1)	λ_2, nm (lg ε_2)	λ_3, nm (lg ε_3)
1 Benzene	184 (4.8)	203 (3.9)	256 (2.4)
2 Phenylcyclopropane	193 (4.7)	220 (3.9)	266 (2.6)
3 Styrene	203 (4.4)	247 (4.1)	286 (2.8)
4 *p*-(Vinylphenyl)-cyclopropane	275 (4.6)	285 (4.0)	290 (2.5)
5  $-\!<^{Cl}_{H}$	292 (4.64)	296 (4.04)	—
6 —Cl_2	295 (4.68)	298 (4.08)	—
7 —CO_2H	296 (4.7)	298 (4.04)	—
8 —CH_2OH	280 (4.6)	290 (3.95)	292 (2.55)
9 —$CO_2C_2H_5$	298 (4.71)	295 (4.3)	297 (2.65)
10  $-CH_2OCH_2-\underset{O}{CH-CH_2}$	279 (4.58)	288 (3.84)	290 (2.54)
11  $-CO_2CH_2-\underset{O}{CH-CH_2}$	293 (4.65)	295 (4.84)	298 (2.3)

2-substituted-1-(*p*-vinylphenyl)cyclopropanes. The compounds under study were synthesized by the procedure [7-9]. They are a new, not examined yet class of compounds in which the substituents at the cyclopropane ring are isolated from the phenyl core by the cyclopropane fragment located in the *para*-position of the benzene ring in the styrene molecule.

The effect of substituents on the vinyl group through the three-membered carbon ring and benzene core were studied by the UV spectra of compounds of 2-substituted-1-(*p*-vinylphenyl)cyclopropanes with a general formula of



~X, where X = H, $-Cl_2$ (gem-dichloro), $-\!<^{Cl}_{H}$ (monochloro), $-CO_2C_2H_5$, $-CO_2H$, $-CH_2OH$, $-CH_2OCH_2-\underset{O}{CH-CH_2}$, $-CO_2CH_2-\underset{O}{CH-CH_2}$

The UV spectra were measured on a SPECORD UV spectrophotometer. Heptane was used as a solvent.

Table 1 lists the wavelengths of the maxima of absorption bands for these synthesized compounds. It is seen that the absorption bands of all compounds under study shift to the long wavelength region. In comparison of the UV spectra of phenylcyclopropane and styrene with the UV spectrum of *p*-(vinylphenyl)cyclopropane (Table 1) one can note a substantial difference due to the ability of the cyclopropane ring to conjugate not only with the phenyl [10] but also vinyl group.

If we assume that the cyclopropane ring is not a part of the conjugated system involving phenyl and vinyl groups, then the UV spectra of styrene would coincide with the spectrum of *p*-(vinylphenyl)cyclopropane. From the table it is seen that the UV spectra of 2-functionally substituted derivatives of *p*-(vinylphenyl)cyclopropane and styrene differ. This difference confirms the ability of the cyclopropane ring to pass the effect of substituents bonded to it and to form a uniform conjugated system involving vinyl, phenyl, cyclopropane, and a substituent.

From the table it follows that the largest changes in the spectra of 2-substituted cyclopropylstyrenes is observed for the compounds containing electron acceptor substituents: $-Cl_2$, monochloro, $-CO_2C_2H_5$, $-CO_2H$. Electron donating substituents (comp. *8*, *10*) result in an insignificant shift to the long wavelength region and an increase in the intensity of bands. The vibrational structure of the benzene band is maintained. The substituents containing the carboxyl group cause a substantial increase in the intensity of absorption bands and their shift to the long wavelength region of the spectrum (comp. *7*, *9,* and *11*). The most "active" substituents lead to band broadening, and in some cases, to a noticeable split of the third band characteristic of styrene.

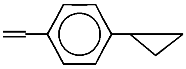
As seen from the table, the UV spectra of *p*-(vinylphenyl)cyclopropane and its 2-substituted derivatives demonstrate a difference of another type that it would be expected if the cyclopropane ring could not pass the effect of the substituent bonded to it.

With regard to the data of the table, it is possible to state that the features of the substituent effects are more pronounced when the substituents are electronegative.

The absorption band shift in the UV spectra of chlorine-containing cyclopropylstyrenes (comp. *5* and *6*) is the most pronounced because of a strong inductive effect of the electronegative chlorine substituent, an increase in the number of chlorine atoms from one to two in the compound causing insignificant changes in the spectra of these compounds.

The formation of a uniform conjugated system is also observed for compounds *10* and *11*. A shortwave maximum (λ_{max} 193 nm) in the spectra of these compounds has a higher intensity as compared to phenylcyclopropane, the maxima shifting to the long wavelength region (279 nm for comp. *10* and 293 nm for *11*). In those cases, when the substituent contains several successive links directly bonded to the cyclopropane ring (comp. *10*), its effect on the conjugation of the whole molecule is insignificant, which is shown by the UV spectrum of this compound, where the shape and intensity of bands slightly differ from those in the spectrum of *p*-vinylphenylcyclopropane. If the carbonyl group is present in the substituent (comp. *11*), and an increase in the absorption intensity is observed, whereas the long wavelength band position (λ_{max} 293 nm) is shifted relative to λ_{max} of *p*-vinylphenyl)cyclopropane (275 nm).

The role of the electronic effect of the epoxygroup is weakly manifested in compounds *10* and *11*. This is likely to be due to the methylene group that is between epoxide and cyclopropane rings in the substituent, which substantially decreases the interaction between them and leads to a small change in the spectrum.

Thus, the UV-spectroscopic data are obtained that allow us to characterize the effect of different substituents X on the system of conjugated π-bonds in the molecule ~X. The main features of the substituent effect on the absorption bands of styrene are noted. The cyclopropane ring is found to be a part of the conjugated system of the whole molecule.

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