# A. S. CHERKASOV

1962

SovietRxiv

chemical structures

Figure 1: chemical structures

## Abstract

## Full Text

## PHYSICAL CHEMISTRY

### A. S. CHERKASOV

# SPECTRAL DETECTION OF THE S-cis AND S-trans ISOMERS OF 2-VINYLANTHRACENE

*(Presented by Academician A. N. Terenin, January 30, 1962)*

From consideration of a scale model of the 2-vinylanthracene molecule it follows that there are two possibilities for the energetically most favorable coplanar arrangement of the conjugated system:

(I) and (II)

Isomerism caused by the partial double-bond character of the single bond located between conjugated double bonds was predicted by Mulliken (1), who proposed designating it as *S*-cis-trans isomerism. For 1,3-butadiene, calorimetric data were used to calculate (2) that the *S*-trans isomer is more stable than the cis isomer (by 2.3 kcal/mol) and that conversion of the *S*-cis isomer into the *S*-trans isomer is associated with overcoming an energy barrier of 2.6 kcal/mol. Apparently, there is no reason to suppose that the mutual transformations of the *S*-cis-trans isomers of 2-vinylanthracene* require energy expenditures substantially different in magnitude from those for the analogous transformations of the isomers of 1,3-butadiene and, consequently, at ordinary temperatures 2-vinylanthracene should constitute an equilibrium mixture of both isomers.

To clarify the question of the existence of isomers of 2-vinylanthracene, we investigated the absorption and fluorescence spectra of this compound. 2-Vinylanthracene was obtained by dehydration of 2-($\alpha$-hydroxyethyl)anthracene** during distillation in the presence of small amounts of $KHSO_4$ in vacuum (1-2 mm Hg) (3). After thorough purification by repeated recrystallization from benzene and chromatography on alumina, 2-vinylanthracene had m.p. 191-192°.

The absorption spectrum of 2-vinylanthracene (Fig. 1)*** has a number of features that distinguish it both from the spectra of the corresponding alkyl derivatives and from the spectra of vinylanthracenes with the vinyl group in a different position. The maximum of its short-wavelength band is shifted to the long-wavelength side relative to the corresponding maximum in the spectrum of anthracene by 3575 $cm^{-1}$, whereas, for example, in 1-, 2-, and 9-methylanthracenes and in 1- and 9-vinylanthracenes this shift amounts to only 250–600 $cm^{-1}$ ⁽⁴⁾. At the same time, the long-wavelength band is shifted by only 325 $cm^{-1}$. This fact is, first, a confirmation of the view that the short-wavelength band in anthracene compounds is associated with oscillations of the electric vector directed along the long axis of the anthracene nucleus ⁽⁵⁾, and, second, indicates—

* Although in 2-vinylanthracene it is not possible to fix a definite arrangement of the double bonds in the anthracene nucleus, form (I) may be designated as the *S*-trans form and (II) as the *S*-cis form, understanding by this the position of the double bond of the vinyl group relative to the longest axis of the anthracene nucleus.

** 2-($\alpha$-Hydroxyethyl)anthracene was obtained by reduction of 2-acetylanthracene with aluminum isopropylate in toluene.

*** We take this opportunity to express our sincere gratitude to V. P. Klochkov for carrying out measurements of the absorption spectra at low temperatures.

indicates a strong interaction between the $\pi$-electrons of the vinyl group and the anthracene nucleus. A second feature in the spectrum of 2-vinylanthracene is the presence of a well-resolved vibrational structure of the short-wavelength band with a frequency characteristic of the long-wavelength band of anthracene and its derivatives (about 1400 $cm^{-1}$). Short-wavelength bands of analogous form in other anthracene derivatives have not been encountered by us up to now.

The most interesting point from the standpoint of the problem posed above is the existence, in the spectrum of 2-vinylanthracene, of a small additional absorption on the long-wavelength branch of the long-wavelength band (Fig. 1). This absorption did not disappear, and its relative magnitude (with respect to the absorption in the region of the maximum of the long-wavelength band) did not change after the most thorough purification of 2-vinylanthracene had been carried out. When the temperature of the solution is lowered, the absorption in the region of this additional band decreases, and at −180° it practically disappears, but it appears again upon subsequent warming of the solution. The temperature dependence of the band under consideration is most naturally explained by the fact that 2-vinylanthracene actually proves to be a mixture of isomers, the equilibrium content of which depends on temperature. The only possible type of isomerism for 2-vinylanthracene is *S*-cis-trans isomerism.

**Fig. 1.** Absorption spectra of 2-vinylanthracene in ethanol. 1 –20°, 2 ––70°, 3 ––140°. The values of $\varepsilon$ for low temperatures are overestimated, since the decrease in the volume of the solution compared with the initial one was not taken into account.

Since, in anthracene derivatives with substituents of the same type, the molar absorption coefficients in the regions corresponding to the absorption maxima are approximately identical, one may suppose that in the isomers of 2-

Fig. 1. Absorption spectra of 2-vinylanthracene in ethanol. 1—20°, 2—−70°, 3—−140°. The values of $\epsilon$ for low temperatures are overestimated, since the decrease in the volume of the solution relative to the initial volume was not taken into account

Figure 2: Fig. 1. Absorption spectra of 2-vinylanthracene in ethanol. 1—20°, 2—−70°, 3—−140°. The values of $\epsilon$ for low temperatures are overestimated, since the decrease in the volume of the solution relative to the initial volume was not taken into account

vinylanthracene they differ little from one another. Then, assuming that band $I'$ in Fig. 1 is the first vibrational band of the spectrum of one of the isomers, and band $I$ is the first vibrational band of the spectrum of the second isomer, one can estimate the ratios of the concentration of the first isomer to the concentration of the second at each of the temperatures studied. From the obtained values of these quantities (293° K —0.14, 203° K —0.06, 133° K —0.03 for solutions in ethanol; 293° K —0.13, 193° K —0.05 for solutions in *n*-heptane), it was found (Fig. 2) that the energy level of the ground state of the first isomer lies approximately 0.9-1 kcal/mol higher than the level of the second isomer. On the basis of the fact that, in anthracene compounds, introduction of a substituent into the $\alpha$-position of the anthracene nucleus usually exerts a stronger influence on the long-wavelength absorption band than introduction into the $\beta$-position [4, 5], and taking into account that the $S$-cis isomer is more similar in its structure to $\alpha$-substituted compounds than is the $S$-trans isomer, one may suppose that the isomer having the more long-wavelength absorption spectrum proves to be the $S$-cis isomer.

Further clear indications of the existence of two isomers were obtained in the study of the fluorescence spectra. As is seen from Figs. 3a and 3b, the form and position of the fluorescence spectrum are very strongly

depends on temperature. It is also clearly seen that in a certain temperature interval it may be represented as the result of the superposition of two spectra, one of which appears in pure form at low temperatures, and the other—in almost pure form at high temperatures. Comparing these data with the results of studies of the absorption spectra, one may conclude that the presence of two fluorescence spectra of 2-vinylanthracene is associated with the existence of two of its isomeric forms. It is most probable that the isomer having the shorter-wavelength absorption spectrum (the trans isomer) also has the shorter-wavelength fluorescence spectrum. This is indicated, for example, by the fact that the distance between the central maxima of the fluorescence and absorption spectra under consideration is 3100 $\text{cm}^{-1}$, which, as was shown ($^{6}$), is characteristic of anthracene derivatives with structured absorption and fluorescence spectra.

**Fig. 2.** *A*—dependence of the logarithm of the ratio of the concentration of the $S$-cis isomer of 2-vinylanthracene to the concentration of the $S$-trans isomer on

Fig. 2

Figure 3: Fig. 2

the reciprocal absolute temperature: 1 and 1′—in the ground state, 2 and 2′—in the excited state; 1 and 2—solutions in ethanol, 1′—2′—solutions in *n*-heptane. *B*—scheme of the arrangement of the energy levels of the *S*-cis ($I'$ and $II'$) and *S*-trans ($I$ and $II$) isomers; the numbers in the figure are energies in kcal/mole.

From Fig. 2 it is seen that a relatively small change in temperature compared with room temperature (20°) is sufficient to cause very substantial changes in the fluorescence spectra. The smallness of the change in the total quantum yield of fluorescence in this case* indicates that the fluorescence quantum yields of the first and second isomers do not differ greatly from each other. In this case, knowing the spectra of each of the isomers, one can estimate their relative concentrations from the composite spectrum. For solutions of 2-vinylanthracene in ethanol the following values were obtained for the ratio of the fraction of the cis isomer to the fraction of the trans isomer: −15°—0.30, 0°—0.72, +20°—1.30, +40° —2.0, +85°—2.9. Somewhat different values of these quantities were obtained for solutions in heptane: −45°—0.16, −18°—0.55, 0°—1.0, 20°—1.8, +80°—4.0. Thus, in the excited state already at a temperature of 20° the concentration of the cis isomer exceeds the concentration of the trans isomer, whereas in the ground state at this temperature it is several times smaller. This fact indicates that in the excited state the *S*-cis configuration proves to be energetically more favorable, and the observed increase in its fraction with increasing temperature indicates that the transition of the *S*-trans isomer into the *S*-cis isomer, occurring during the lifetime of the excited state, is associated with overcoming an activation barrier. The dependence of the logarithm of the relative concentration of the isomers on the reciprocal values of the absolute temperature (Fig. 2) is obtained as close to linear**. Calculated from from the slope of the curves the activation energy was found to be 4.5–5 kcal/mole. Taking into account that the absorption and fluorescence spectra of the *S*-cis isomer are shifted relative to the corresponding spectra of the *S*-trans isomer by 800–900 $\text{cm}^{-1}$ (about 2.3 kcal/mole), the relative positions of the levels of the *S*-cis and *S*-trans isomers may be represented in the form of the scheme shown in Fig. 2.

Thus, if in the ground state of 2-vinylanthracene the equilibrium is shifted toward the *S*-trans isomer, then in the excited state the existence of the *S*-cis isomer is energetically more favorable, and at temperatures sufficient to overcome the activation barrier during the lifetime of the molecules of the *S*-trans

---

* When the temperature is raised from 20 to 80°, the yield decreases by 15%.

** Deviations from linearity at high temperatures may be associated with the attainment of transformation rates that ensure the establishment, during the lifetime of the excited state, of concentrations close to equilibrium.

isomer in the excited state, their conversion into the $S$-cis form occurs. The existence of this conversion process is also confirmed by the fact that, when fluorescence quenchers are added to the solution (we used KI and $n$-toluidine for this purpose), the fluorescence of the $S$-cis isomer is quenched to a greater extent than the fluorescence of the $S$-trans isomer, and the fluorescence spectrum approaches in appearance the spectrum of the $S$-trans isomer (Fig. 3 ). The greater quenching of the fluorescence of the $S$-cis isomer follows directly from the possibility of its additional quenching at the $II'$ level (Fig. 2).

**Fig. 3.** Fluorescence spectra of 2-vinylanthracene. **a** –in ethanol: 1 ––85°, 2 ––20°, 3 –0°, 4 ––50°, 5 ––183°; –in $n$-heptane: 1 –80°, 2 ––20°, 3 ––18°, 4 ––45°; –in ethanol containing potassium iodide (temperature 20°): 1 –0, 2 –$3 \cdot 10^{-2}$ mole/l, 3 –$5 \cdot 10^{-2}$ mole/l.

Received
12 I 1962

## CITED LITERATURE

1. R. S. Mulliken, Rev. Mod. Phys., **14**, 265 (1942); J. Chem. Phys., **7**, 121 (1939).
2. J. G. Aston, G. Szasz et al., J. Chem. Phys., **14**, 67 (1946); A. D. Walsh, Nature, **157**, 768 (1946).
3. E. G. E. Hawkins, J. Chem. Soc., 1957, 3858.
4. A. S. Cherkasov, *Optics and Spectroscopy*, **6**, 496 (1959).
5. R. N. Jones, Chem. Rev., **41**, 353 (1947).
6. A. S. Cherkasov, T. M. Vember, *Optics and Spectroscopy*, **1**, 663 (1956); A. S. Cherkasov, ZhFKh, **29**, 2209 (1955).

*Note: Figure translations are in progress. See original paper for figures.*

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*