

2-(2-Hydroxyphenyl)benzotriazoles. IV. Ionization constants

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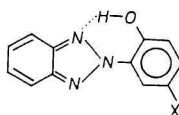
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Received 10 July 1974

Ionization constants of some 2-(2-hydroxy-5-X-phenyl)benzotriazoles were measured by the ultraviolet spectrophotometric method. A linear correlation was found between the ionization constant values and σ_p constants of substituents X ($\rho = -2.6$) and also between the wavenumber of the stretching vibration of the OH bond and the pK_a values ($\rho = +41.1$).

2-Phenylbenzotriazole satisfactorily absorbs in the near ultraviolet region [1]. Introduction of a hydroxyl group in *o*-position to nitrogen atom of the triazole ring resulted in formation of a new absorption band at about 334 nm [2]. This feature of 2-(2-hydroxyphenyl)benzotriazole *I* and its derivatives is often evaluated in using them as absorbers for ultraviolet beams of unwanted wavelength in various substances, mostly of macromolecular character [3–5].

A series of derivatives of compound *I* (Scheme 1, X = H) was synthesized and the effect of substituents investigated in the infrared and ultraviolet spectral range [2, 6].



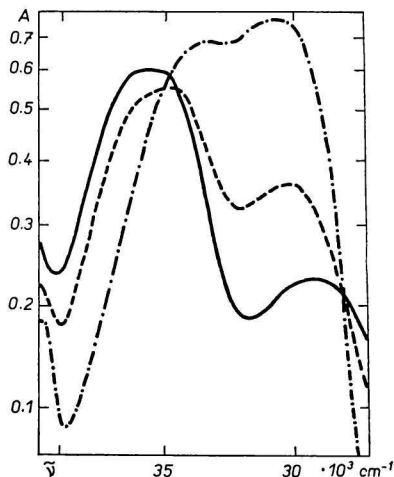
Scheme 1

The dependence of the stretching vibration value of the OH group with an associated hydrogen was found to be linear on the σ_p constants; the effect of substituents was seen both in the intensity and position of the absorption band in the ultraviolet region.

To get further information on the electron density of the OH bond, ionization constants pK_a of some 2-(2-hydroxy-5-X-phenyl)benzotriazoles, where X = H (*I*), OCH_3 (*II*), CH_3 (*III*), Br (*IV*), $CON(C_2H_5)_2$ (*V*), were determined by means of ultraviolet spectroscopy. The selection of compounds was restricted by their ability to form solutions in suitable solvents at a concentration required for the ultraviolet measurement.

Fig. 1. Ultraviolet spectrum of substance I.

- — — Measured in ethanol; concentration 6×10^{-5} M.
 - - - Measured in 50% ethanol at pH 9.7.
 ——— Measured in 50% ethanol at pH 12.0.



Absorption band, which varied in the 335 to 365 nm region in dependence on the character of the substituent X and whose intensity sensitively reflected the change of pH of the medium in which the ultraviolet spectrum was measured, was selected for the pK_a value determination. The absorbance of this absorption band is therefore related to the ionization degree of the OH bond (Fig. 1).

Experimental

Ultraviolet spectra were measured with a VSU 1 (Zeiss Jena) and UNICAM SP 700 apparatuses in 50% aqueous methanol, in a 1-cm quartz cell at 21°C; concentration 6×10^{-5} M. Britton—Robinson buffer solution, concentration 2×10^{-2} M, was employed. The ionization constants were measured at a constant ionic strength adjusted by addition of sodium perchlorate. The pH values were read on the Radiometer Copenhagen NV using glass and calomel electrodes at 21°C. Compounds I—V were measured at six pH values varying within the ± 0.1 to 0.2 pH interval from the calculated pK_a value.

Infrared spectra were measured with a Zeiss Jena UR-10 spectrometer in carbon tetrachloride (6×10^{-3} M) in a 1-cm quartz cell.

The pK_a values were calculated according to equation

Table 1

Characteristic values of compounds under investigation

| Compound | λ [nm] Wavelength employed | $\nu(\text{OH})$ [cm^{-1}] | pK_a | σ_p |
|----------|--|--|--------|------------|
| I | 335 | 3180 | 9.40 | 0.000 |
| II | 365 | 3230 | 9.92 | -0.268 |
| III | 340 | 3205 | 9.83 | -0.170 |
| IV | 340 | 3175 | 8.76 | 0.232 |
| V | 335 | 3135 | 8.40 | 0.350 |

$$\text{p}K_{\text{a}} = \text{pH} - \log \frac{A_{\text{x}} - A_1}{A_2 - A_{\text{x}}},$$

where A_1 = absorbance of the nonionized form,

A_2 = absorbance of the totally ionized form,

A_{x} = absorbance of the particular form at a certain pH.

The measured values of substances I–V (Table 1) are linearly dependent on the σ_{p} constants of substituents X with $\rho = -2.6$ ($r = -0.994$). The stretching vibrations of the OH bond are also in a linear correlation with the $\text{p}K_{\text{a}}$ values ($\rho = +41.1$, $r = 0.935$).

References

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Translated by Z. Votický