2-Aryl derivatives of condensed five-membered *N*-heterocyclic compounds. V. Photolysis of 2- and 4-substituted phenols and naphthols in benzene solution

J. DURMIS and M. KARVAŠ

Research Department, Chemical Works of J. Dimitrov,
810 01 Bratislava

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Photochemical stability of 2- and 4-substituted phenols containing 2-(4,5)-aryleneazolyl, 2-indolyl, and benzoyl substituents as well as of benzotriazolylnaphthols in benzene solutions was investigated. It was found that, from among the compounds studied, 2-hydroxybenzophenone and 2-(2-benzotriazolyl)phenol were photochemically most stable. The quantum yield of the photolytic decay decreased by about one order of magnitude in the presence of an intramolecular hydrogen bond.

One of the most important properties of a polymer photostabilizer as reported *e.g.* in [1—3], is its stability to ultraviolet radiation. In winter the minimum wavelength of the sunlight is usually greater than 300 nm. The shortest measured wavelength of the light reaching the earth's surface is 286.3 nm [4]. From these data follows the wavelength range in which the photostabilizer itself should be stable.

Already *Gantz* and *Summer* [5] found that 2-hydroxybenzophenones exhibited exceptional photostability when irradiated in a film of poly(methyl methacrylate) or of cellulose acetate. Contrary to this, *Goth* [6] found that 2-hydroxybenzophenone decomposes predominantly to hydroquinone when irradiated in a PVC film or in methanol solution. It has been also found that the substituents affect the photostability of 2-hydroxybenzophenone at 300—400 nm only to a small extent and that the radiation having the wavelength shorter than 300 nm causes rapid decomposition of these compounds [7]. More detailed studies on the photoreactivity of the 2-hydroxybenzophenone derivatives in solution can be found in the works of *Porter* [8, 9]. The low reactivity of 2-hydroxybenzophenone is ascribed to a reversible enolization [10, 11] and to a "charge-transfer" configuration in its excited state [12]. The role of intramolecular hydrogen bond in the process of deactivation of the excited state in 2-hydroxybenzophenone has not yet been explained [12].

Merrill and *Bennett* [13] studied the effect of the position of 2-benzotriazolyl substituent on the photochemical stability of acetanilides. They found that the *ortho* isomer, having strong intramolecular hydrogen bond, is photochemically more stable than the non-hydrogen-bonded *meta* and *para* isomers. Also the high photochemical stability of 2-hydroxyphenylquinazolines is ascribed to the existence of a strong intramolecular hydrogen bond [14].

The aim of the present study was to determine the photostability of phenolic compounds containing five-membered nitrogen heterocycles in the molecule (Schemes 1—4) and to elucidate the effect of the intramolecular hydrogen bond on the photochemical stability of substituted phenols containing different proton acceptors participating in the formation of the intramolecular hydrogen bond.

Experimental

A high-pressure mercury lamp (Type TQ 120 K; Original Hanau Quarzlampen, GMBH) equipped with a quartz jacket for water cooling was immersed together with the photolysis flasks in a thermostating bath at 25 ± 1°C. The quartz photolysis flasks were shielded by an aluminium foil in their upper part. During photolysis, the reaction mixture was bubbled through with nitrogen saturated by the used solvent. 10^{-4} M Substrate solution (30 ml; 10^{-3} M solutions with benzophenone derivatives) was pipetted into each reaction flask. The concentrations were chosen so that their maximum transparency at the beginning of photolysis was 1%. By the persistent shielding of the upper parts of the reaction flasks the overall irradiated surface of the samples was kept constant in spite of the volume decrease caused by sample withdrawal.

In the taken samples the absorbancy at the chosen wavelengths, usually at the absorption maximum of the longest wavelength, was measured. The thickness of the irradiated sample (light path) was 3 cm. Ultraviolet absorption spectra were measured on a single-beam non-recording VSU-1 (Zeiss, Jena) spectrophotometer.

The light intensity of the used mercury lamp was measured by means of a ferrioxalate

Table 1

Calculation of the effective quantum yield, Φ Fe^{2+}, for 0.03 M-$K_3Fe(C_2O_4)_3$ and a high-pressure mercury lamp TQ 120 K

λ [nm]	r_{λ_i} a) [mW]	$n_{\lambda_i} \cdot 10^{-15}$ b) [quanta s^{-1}]	y_i c)	$n_{\lambda_j} \cdot y_i \cdot 10^{-5}$ [quanta s^{-1}]	$x_{\lambda_i} \cdot 10^2$ d)	Φ Fe$^{2+}_{\lambda_i}$ e)	$x_{\lambda_i} \cdot \Phi$ Fe$^{2+}_{\lambda_i}$
302	72	109.8	1	109.8	0.456	1.24	0.00565
313	912	1448	1	1448	6.01	1.24	0.07450
334	288	484	1	484	2.01	1.23	0.02470
336	4800	8840	1	8840	36.8	1.21	0.44500
405/8	2448	5000	1	5000	20.8	1.14	0.23700
436	3264	7150	0.954	6820	28.3	1.01	0.28600
546	4944	13680	0.035	478	1.99	0.15	0.00298
577/9	4704	13700	0.064	876	3.64	0.013	0.00047
							Φ Fe^{2+} = 1.07630

a) Relative performance of the TQ 120 K lamp at the wavelength λ_i; taken from literature data [17].

b) Relative number of emitted quanta: $n_{\lambda_i} = 10^4 \cdot r_{\lambda_i} \cdot \lambda_i / h \cdot c$, where λ_i is the wavelength in cm, $h = 6.625 \times 10^{-27}$ erg s, and $c = 3 \times 10^{10}$ cm s^{-1}.

c) Fraction of the radiation absorbed by 3 cm layer of potassium ferrioxalate.

d) $x_{\lambda_i} = n_{\lambda_i} \; y_i / \Sigma n_{\lambda_i} \cdot y_i$.

e) Cited from [18].

actinometer [15, 16]. Radiation dose was calculated from the known $N_{\mathrm{Fe}^{2+}}$ and from the quantum yield of Fe^{2+} using the formula

$$I_0^i = \frac{N_{\mathrm{Fe}^{2+}}}{\Phi\,\mathrm{Fe}^{2+} \cdot t}, \tag{1}$$

where I_0^i is the radiation dose (quanta s^{-1}), $\Phi\,\mathrm{Fe}^{2+}$ is the effective quantum yield of Fe^{2+} formation, t is the time of irradiation (s), and $N_{\mathrm{Fe}^{2+}}$ is spectrophotometrically determined number of Fe^{2+} ions formed [15]. The effective quantum yield of Fe^{2+} ions was 1.076 under the conditions used; the method of its calculation is demonstrated in Table 1.

The mercury lamp used as a radiation source had relatively stable performance and was continuously in operation. For the calculation of the quantum yield of photodestruction of the compounds studied an average value of light intensity, $I_0^i = (8.8 \pm 0.9) \times 10^7$ quanta s^{-1}, was taken in all experiments. The quantum yield of the photodestruction of the compounds studied was calculated using equation

$$Q = \frac{n}{N_{\mathrm{r}} \; t}, \tag{2}$$

where Q is the quantum yield of photodestruction, n is the number of molecules decayed in the time t (s), and N_{r} is the actual number of quanta absorbed by a single molecule per second.

The number of molecules decayed in the time t was determined by measuring the decrease of absorbancy of the given sample with time. This function is linear in the first phase of the photodecay (Figs. 1 and 2). For the calculation of n, the time t_{70} during which the absorbancy of the irradiated solutions decreased to 70% of the original value, or the time during which 30% of the studied compound decayed, was determined. The calculation was simplified by the fact that in all cases the products of photodestruction absorb weakly at 300–400 nm (Figs. 3 and 4). These absorbancies were neglected in the calculations.

The actual number of the effective quanta, N_{r}, was calculated from the total number of quanta N radiated into the photolysis space, as determined by the ferrioxalate actino-

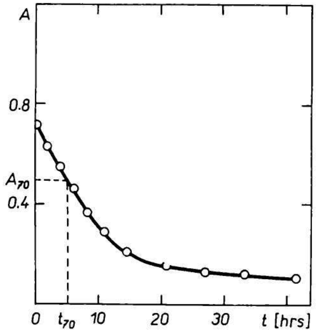


Fig. 1. Time change of absorbancy of 4-(2-benzoxazolyl)phenol in benzene solution ($c = 2.5 \times 10^{-5}$ M, $\lambda = 307$ nm, $d = 1$ cm) in the course of irradiation.

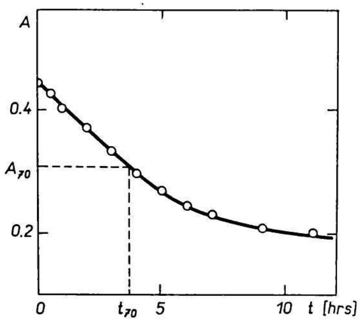


Fig. 2. Time change of absorbancy of 2-(2-indolyl)phenol in benzene solution ($c = 2.5 \times 10^{-5}$ M, $\lambda = 318$ nm, $d = 1$ cm) in the course of irradiation.

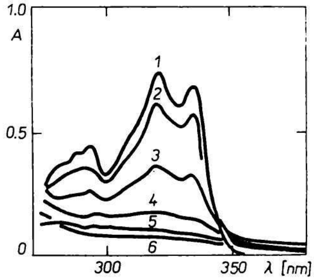


Fig. 3. Ultraviolet absorption spectra of 2-(2-benzimidazolyl)phenol in benzene solution ($c = 3.33 \times 10^{-5}$ M, $d = 1$ cm) before irradiation (curve *1*) and after different time of irradiation: *2.* 3 hours; *3.* 8 hours; *4.* 12 hours; *5.* 24 hours; *6.* 48 hours.

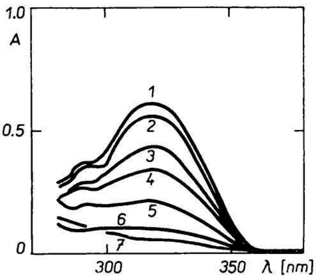


Fig. 4. Ultraviolet absorption spectra of 2-(2-indazolyl)phenol in benzene solution ($c = 3.33 \times 10^{-5}$ M, $d = 1$ cm) before irradiation (curve *1*) and after different time of irradiation: *2.* 24 hours; *3.* 76 hours; *4.* 118 hours; *5.* 168 hours; *6.* 210 hours; *7.* 264 hours.

meter, and from the u.v. absorption spectra of the photolyzed compounds in benzene. An example for the calculation of N_r is demonstrated in Table 2. The N_r values of all the compounds studied are summarized in Table 3.

The decrease of the fraction of absorbed radiation, *i.e.* the decrease in the actual number of absorbed quanta, caused by the decrease of absorbancy with time was neglected in the calculations of Q. The maximum decrease of the number of absorbed quanta (Tab. 2)

Table 2

Calculation of the effective number of absorbed quanta, N_r, for the benzene solution of compound *VII*

λ [nm]	Y_{λ_i} a)	x_{λ_i} b)	$N_{\lambda_i} \cdot 10^{-17}$ c) [quanta s^{-1}]
302	0.99	0.46	0.0397
313	1.00	6.01	0.5300
334	1.00	2.01	0.1770
366	1.00	36.80	3.2400
405	0.56	20.80	1.0260
436	0.00	28.30	0.0000
546	0.00	1.99	0.0000
577	0.00	3.64	0.0000

$$N_r = \sum_0^i N_{\lambda_i} = 5.0127 \cdot 10^{17}$$

a) Fraction of the radiation absorbed by 10^{-4} M solution of the compound *VII* in benzene.

b) The values taken from Table 1.

c) Fraction of actually absorbed quanta at the wavelength λ_i, $N_{\lambda_i} = N x_{\lambda_i} Y_{\lambda_i}$, where N is the total number of quanta radiated into the photolysis space, $N = I_0^i$.

Table 3

Quantum yields of photolytic decay

Compound	λ[a] [nm]	$N_r \cdot 10^{-17}$[b] [quanta s^{-1}]	t_{70}[c] [hours]	Q[d] [mol einstein^{-1}]
I	335	3.45	$\gg 700$	$< 6.4 \times 10^{-7}$
II	318	2.89	8.2	6.3×10^{-5}
III	328	1.85	74	1.1×10^{-5}
IV	307	0.82	23.2	7.9×10^{-5}
V	349	3.99	380[f]	1.2×10^{-7}
VI	344	3.90	1.8	$2.1 \quad 10^{-4}$
VII	356	5.01	75	4.0×10^{-6}
VIII	323	4.37	0.5	6.9×10^{-4}
IX	322	0.79	108	1.8×10^{-5}
X	307	2.28	5.2	1.3×10^{-4}
XI	320	0.75	5.0	4.0×10^{-4}
XII[e]	—	—	—	—
XIII	320	1.30	6.0	1.9×10^{-4}
XIV[e]	—	—	—	—
XV	340	3.55	13.6	13.1×10^{-5}
XVI	308	0.86	4.2	8.7×10^{-4}
XVII	318	1.54	3.7	3.0×10^{-4}
XIX	340	3.84	$\gg 700$	$< 5.6 \times 10^{-7}$
XX	280	2.78	2.2	2.4×10^{-4}

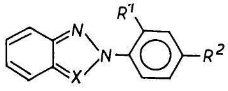
a) Wavelength at which the decrease of absorbancy was measured.
b) Actual number of quanta absorbed by the solution of the respective compound.
c) Time needed for decrease of absorbancy to 70% of the original value.
d) Quantum yield of the photolytic decay.
e) Too low solubility in benzene.
f) The value corresponds to t_{90}.

has never exceeded 4% during the time t_{70}. This implies that in an extreme case the actual number of absorbed quanta was by less than 3% lower than the value taken into the calculations of Q. Such an error is much smaller than the overall 20% error occurring in the estimation of the quantum yield.

The compounds *I*—*XX* were described previously [19].

Results and discussion

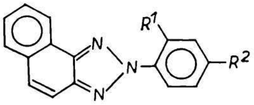
A survey of the quantum yields of 2- and 4-substituted phenols (Schemes 1—5) is given in Table 3. This table presents the times required for 30% decomposition of the individual compounds. It also shows that the quantum yields of all the studied compounds were



I. X = N, R^1 = OH, R^2 = H; *II*. X = N, R^1 = H, R^2 = OH; *III*. X = CH, R^1 = OH, R^2 = H; *IV* X = CH, R^1 = H, R^2 = OH.

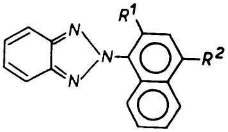
Scheme 1

of 10^{-4} order of magnitude or lower. 2-Hydroxybenzophenone and 2-(2-benzotriazolyl)-phenol (*I*) represent extreme exceptions; their composition and u.v. spectra did not change even after 700 hours of irradiation. These results confirm that the commercially produced derivatives of 2-hydroxybenzophenone and of 2-(2-benzotriazolyl)phenol which are known as the best and most widely used u.v. absorbers in organic materials, especially in plastics, are exceptionally stable from the photochemical point of view as well. This property makes them suitable for the use as photostabilizers. In the group of 2-substituted phenols, 2-(2-naphtho-[1,2-*d*]triazolyl)phenol (*V*) and 1-(2-benzotriazolyl)naphthol (*VII*)



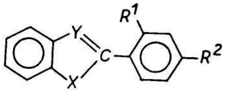
V. R^1 = OH, R^2 = H; *VI*. R^1 = H, R^2 = OH.

Scheme 2



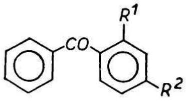
VII. R^1 = OH, R^2 = H; *VIII*. R^1 = H, R^2 = OH.

Scheme 3



IX. Y = N, X = O, R^1 = OH, R^2 = H; *X*. Y = N, X = O, R^1 = H, R^2 = OH; *XI*. Y = N, X = NH, R^1 = OH, R^2 = H; *XII*. Y = N, X = NH, R^1 = H, R^2 = OH; *XIII*. Y = N, X = N–CH_3, R^1 = OH, R^2 = H; *XIV* Y = N, X = N–CH_3, R^1 = = H, R^2 = OH; *XV*. Y = N, X = S, R^1 = OH, R^2 = H; *XVI*. Y = N, X = S, R^1 = H, R^2 = OH; *XVII*. Y = CH, X = NH, R^1 = OH, R^2 = H; *XVIII*. Y = CH, X = NH, R^1 = H, R^2 = OH.

Scheme 4



XIX. R^1 = OH, R^2 = H; *XX*. R^1 = H, R^2 = OH.

Scheme 5

were most stable. In the group of 2-substituted phenols containing heterocyclic substituents the greatest photostability exhibited the compounds containing 1,2,3-triazole ring. It can be further generalized that the compounds having quinoid structure are more stable than the other compounds having an aromatic heterocyclic substituent. Since, in spite of having an aromatic structure, 1-phenylbenzotriazole and its derivatives are photochemically relatively unstable [20]; the photochemical stability of 2-hydroxy compounds *I*, *III*, *V*, and *VII* can be ascribed to the delocalization of electrons in their molecules. It was found that in compounds containing 1,2,3-triazole ring the presence of naphthalene structure negatively influences the photostability in contrast to the analogous compounds containing benzene ring instead of the naphthalene structure in the molecule. At the same time, it can be assumed that it is not only the quinoid structure of 2-phenylbenzotriazole derivatives but also their symmetry that can contribute to the high photostability of these compounds. Distortion of the molecular symmetry, either by introducing naphthalene or by simple replacing a nitrogen atom by CH group, leads to a decrease in photochemical stability.

The photochemical stability of 2-substituted phenols with aromatic structure of the heterocyclic substituent (Scheme 4) is lower by at least one order of magnitude. In the group of these compounds, the most stable is 2-(2-benzoxazolyl)phenol (*IX*) having relatively symmetric structure. Almost the same photostability has 2-(2-benzothiazolyl)-phenol (*XV*). The compounds possessing secondary or tertiary amino groups in their molecules (*XI*, *XIII*, *XVII*) are the least stable to the u.v. light.

A similar situation can be found also in 4-substituted phenols. The compounds having 2-benzotriazolyl and 2-indazolyl substituents (*II*, *IV*) are most stable from among the phenols tested. Apparently, their stability can be ascribed to their quinoid structure. The 4-substituted phenols containing naphthalene ring in the molecule are, in contrast to the similar 2-substituted phenols, very little stable. The compound *VIII* is the least stable among all the compounds tested (except for *XVI*).

Excepting 2- and 4-substituted 2-indolylphenols, the quantum yield of the photolytic decay with all 4-substituted phenols was by at least an order of magnitude higher than that with 2-substituted phenols. In all 2-substituted compounds, except for 2-(2-indolyl)-phenol, the formation of a strong intramolecular hydrogen bond was found to occur in nonpolar medium [21]. From the above observation it follows that the presence of an intramolecular hydrogen bond positively influences the photochemical stability of the given compound. As early as in 1955 *Shigorin* and *Dokunikhin* [22] stated that the important property of the strong intramolecular hydrogen bonds with π-electron interaction is the ability to absorb the energy several times greater than would be sufficient for their cleavage. The absorbed energy is spread through the conjugated π-bonds over the whole molecule. *Durvasula* and *Lamberti* [23] discuss the positive influence of an intramolecular hydrogen bond on the u.v. photostability of compounds. A comparison of the relative strengths of the intramolecular hydrogen bonds in the individual 2-substituted phenols [21] with their quantum yields of the photolytic decay shows that a linear correlation between the strength of the hydrogen bond and the photochemical stability of the given compound cannot be found. This fact is in contradiction with the statement [24] about the photostabilizing activity of 2-hydroxybenzophenone in polyethylene. On the other hand, it is interesting that in the least photoreactive compounds (*I* and *XIX*) the strong intramolecular hydrogen bond present in the nonpolar medium is completely broken in dimethyl sulfoxide [25]. In these compounds the hydrogen bond is the least stable to the attack of different proton-accepting reagents. It remains to answer the question by which mechanism the intramolecular hydrogen bond influences the photoreactivity. *O'Connell*

[26] has shown that even the weak intramolecular hydrogen bond in 2-hydroxy-4,6-di-*tert*-butylbenzophenone considerably influences the photoreactivity.

Merrill and *Bennett* [13] found that in 2-(2-benzotriazolyl)acetanilides the intramolecular hydrogen bond substantially influences mainly the internal conversion from excited singlet to ground state or, in other words, it increases the fraction of energy released as a heat in the course of deactivation of the excited state. Possibly this explanation is valid generally for the intramolecular hydrogen bonds. It is sure, however, that the presence of a strong intramolecular hydrogen bond decreases the photoreactivity of all the compounds under study. It is apparently related to the fact that the intramolecularly hydrogen-bonded compounds have smaller tendency to enter the chemical reactions [27].

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