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Prediction of the Photofading of Selected Derivatives of 5-(4-X-Phenylazo)-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone: Theoretical Studies, Comparison of AM1 and PM3 Methods

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Abstract

We analysed the photooxidation reaction in the electro-($^1O_2$) and nucleophilic ($O_2^{\bullet-}$) reaction of 2-pyridone azo derivatives. First, we calculated the energy (enthalpies) of tautomers formation, which is a measure of durability and the probability of their formation. We performed the light fastness calculations of the monoazopyridone dyes. Using the semi-empirical methods of quantum chemistry AM1 and PM3, the reactivity indicators of superdelocalisability ($S_r^{E(N)}$) and the electron density distribution in ground state on the highest occupied HOMO orbital and the lowest unoccupied excited state LUMO in 2-pyridone phenylazo derivatives were calculated. Superdelocalisability coefficients enable the stability to oxidising agents of various chemical molecules depending on the tautomeric forms in which they may occur. The results of the electron density calculations at the HOMO and LUMO boundary orbitals allow to determine the tendency to electrophilic attack with singlet oxygen $^1O_2$ or nucleophilic attack of the superoxide anion $O_2^{\bullet-}$ on a specific atom in the molecule. The structure of the dyes was optimised with MM+, MD and AM1 or PM3 until a constant energy value was achieved with a convergence criterion of 0.01 kcal/mol.

Keywords

Photochemical Degradation, AM1 and PM3 Methods, Boundary Orbitals Electron Densities, Electrophilic and Nucleophilic Reaction, HOMO and

LUMO Orbitals

1. Introduction

Azo dyes are a large group of dyes constituting about 50% of all commercial brands [1]. Their wide application results from their relatively simple synthesis and a wide range of obtained colors. Azo dyes are used for dyeing fabrics, leathers, cellulose, paper as well as in the food and cosmetics industries. In addition, they exhibit antibiotic, antifungal and anti-HIV properties. They are also used in photosensitive photovoltaic cells, biological research on fluorescent probes, photonics, non-linear optical devices, and polarising filters [2]-[4].

Azo derivatives of 2-pyridone are used as disperse dyes for polyester and nylon [5] and in printing inks. They have been tested in thermal transfer printing processes and in the production of color filters [6]. Their fluorescent behavior has also been described. Dyes based on pyridone groups have been tested as antioxidant, antimicrobial and antitumor agents [3] [7]-[9].

Azo derivatives of pyridone have been known since around 1960. Arylazopyridone derivatives are a particularly important class of dyes, and their use is considered one of the most important achievements of dye chemistry [10] [11].

The success of pyridone dyes is due to the simplicity of their synthesis, their ability to couple with many diazo compounds, high coefficients of molar extinction and relatively high lightfastness [7] [12] [13].

The color of monoazo derivatives is limited to the absorption range from greenish-yellow to orange, in a few cases to red [2] [10] [14] [15]. They are characterised by high tinctorial strength, comparable to some azonaphthols.

Theoretically, 2-pyridone azo dyes can occur in several tautomeric forms, with the hydrazone form predominating [16]-[18]. The hydrazone form of the dye is characterised by a bathochromic shift of the absorption bands in relation to the azo tautomer [19]. Tautomerism [AZO-HYD] significantly affects the rate of decomposition of dyes in the photochemical reaction [20]-[23]. However, due to the existence of the equilibrium [HYD ⇆ anionAZO] at different pH values, a significant technological problem of discoloration in the dyeing process may occur [24] [25].

The substituents influence the color of azo and hydrazone forms in various ways. In azo tautomers, the acceptor substituents (E_A) in the diazo compound cause the bathochromic effect, while the electron donating substituents (E_D) cause the hipsochromic effect.

For hydrazone tautomers, the effect is reverse. Owing to this, it is possible to determine the tautomeric form, in which a given dye occurs. From the point of view of the valence bond theory, AZO dyes are characterised by significant differences between the ground and excited states. They usually occur in the form of a neutral aromatic structure, while in the excited singlet state this form is lost and

the HOMO-LUMO energy differences are smaller [16] [19].

In the tautomeric form of AZO, the phenylazo group is a substituent of E_A. Thus, the E_A groups stabilised the excited state, while the E_D groups destabilise it. Photoreduction of azo dyes by UV radiation causes the formation of hydrazine radicals, which in the disproportionation reaction cause the production of appropriate amines and iminoquinones [26].

Reaction intermediates are unstable, have a short lifetime and are present in low concentrations. These features prevent their accumulation and do not affect the further course of the reaction.

Despite various doubts, the proposed mechanism of reduction by reducing azo bonds is currently considered to be confirmed by the results of experimental studies [27], and derivatives containing nitro groups undergo photoreduction to a nitroso group and then to an amino group [28] [29].

As research shows, the oxidation rate of dyes depends on their structure [30] [31] and the nature of the substituents [32]. It has been confirmed, for example, that by oxidation with the Fe^{3+}-EDTA-H_2O_2 system (derivatives with -CH_3, -OCH_3, -Cl substituents were tested), Cl derivatives oxidised and discolored the fastest [32]. The analysis was performed using the DFT method [31]. Research results suggest that the photodegradation of o-hydroxyazo dyes takes place in the hydrazone form, and singlet oxygen is the oxidant [33] [34]. This leads to the hyperoxide form, which decomposes by homolysis or heterolysis to quinone and to the ionic form of the diazonium residue (X-p-diazonium ion).

The C-N bond cleavage mechanism was first proposed by Spadano *et al.* [35]. A mechanism involving bond cleavage has been proposed based on the analysis of the decomposition of azo dyes by hydroxyl radicals ($OH^{\bullet}$). In experimental studies, it has been found that the attack of the radical occurs on the carbon atom attached to the azo bond. The main decomposition products in the oxidation process are benzene derivatives [32] [36]-[38].

Initially, the reaction leads to the formation of a radical, a molecule of phenyldiazene and phenol, followed by its decomposition into a molecule of nitrogen and a phenyl radical.

The above mechanism has been proposed for the Fenton reaction Fe^{3+}/H_2O_2, in which the reactant is the hydroxyl radical $OH^{\bullet}$, and the reaction products are decay and oxidation products. However, in most cases, the o-hydroxyazo dyes are mainly in the hydrazone form and a different bond cleavage of the C-N mechanism should be proposed.

The light fastness of dyes has been the subject of many studies. The most numerous concerned azo dyes [30] [31] [39]-[55]. The properties of dyes on the dyed material depend on:

- their construction;
- aggregation capacity;
- azo-hydrazone equilibria;
- polarity of substituents, electron donor (E_D) or electron acceptor (E_A);

- type of dyed fibers [56] [57].

It was noticed that the increase in dye resistance results from the presence of E_A substituents in their molecules, which become unstable to oxidation. However, this theory raises several objections [40].

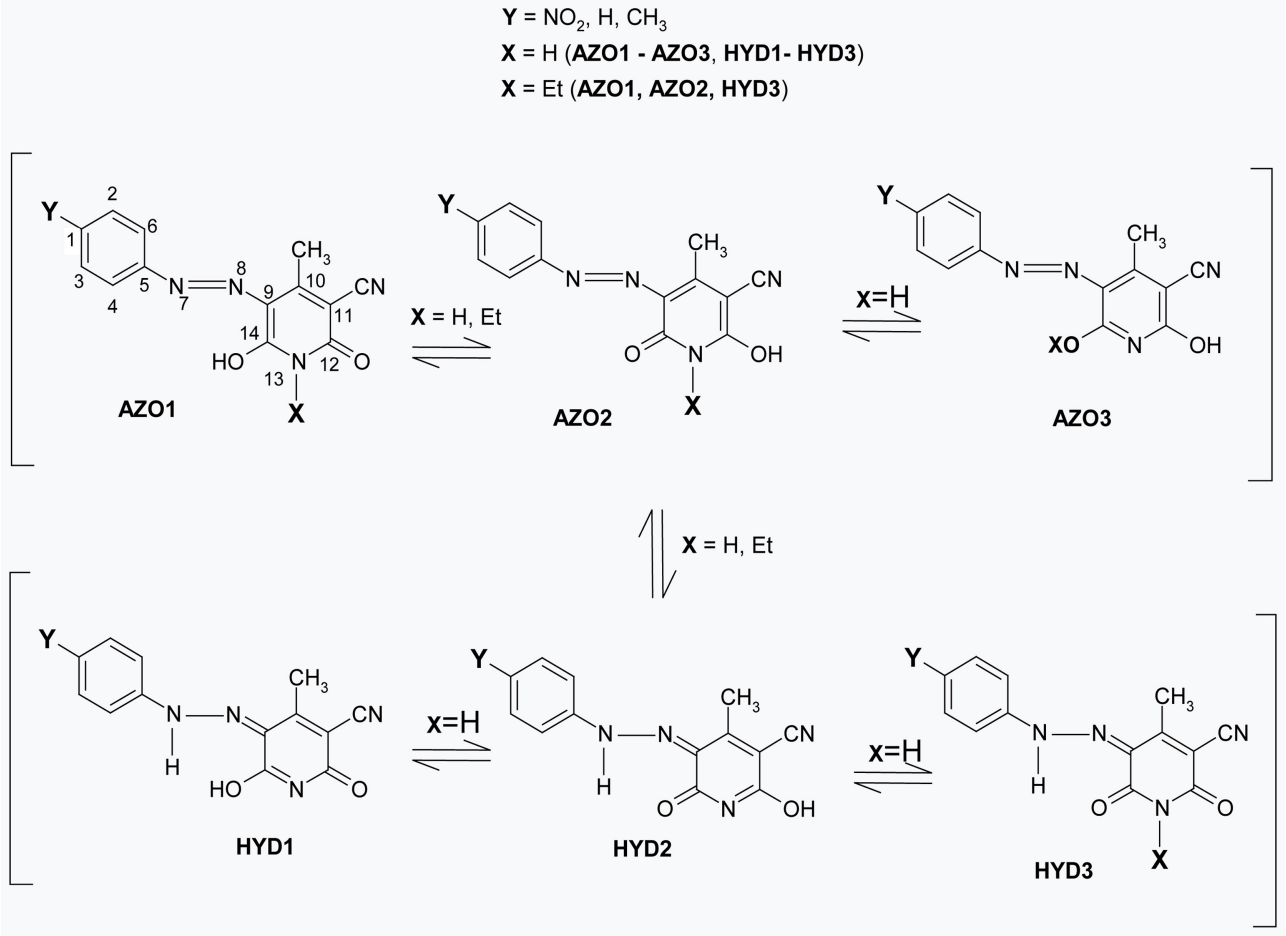

Figure 1. Tautomeric azo-hydrazone equilibria of 5-(4-X-phenylazo)-3-cyano-1-(H or C_2H_5)-6-hydroxy-4-methyl-2-pyridone derivatives.

Molecular orbital (MO) calculations provide insight into the photo-oxidation reaction process, depending on the electronic properties of the molecules [58]. Most of them were carried out in dyes containing azo groups [59] [60]. To understand the influence of the dye structure on lightfastness, the identification of reactive sites in a particular dye was addressed first [61] [62].

The rapid discoloration and degradation into small particles indicate that the reaction may proceed via N=N bond cleavage. The use of Fukui indices, which determine the reactivity of individual atoms of the molecule, is very helpful in explaining this phenomenon. The presence of the hydrazone tautomer seems to be more conducive to the C9-N8 bond cleavage mechanism (**Figure 1**).

The aim of our research was.to calculate and compare the lightfastness of probable tautomeric forms of azo dyes, NH- and NEt-2-pyridone derivatives using the

AM1 and PM3 methods. These two types of dyes exist in an equilibrium of azo (AZO1, AZO2, AZO3)—hydrazone (HYD1, HYD2, HYD3) and lactam (AZO1, AZO2, HYD3)—lactim (AZO3, HYD1, HYD2) tautomeric forms.

Molecular orbital (MO) calculations were performed to gain insight into the process of photo-oxidation with oxygen in electrophilic and nucleophilic reactions. The results of the MO calculations were used to obtain the electron density of orbital in the ground HOMO and excited LUMO orbitals ($f_r^{E(N)}$), and determination of the place where the aerobic decomposition of azo dyes took place using singlet oxygen $^1O_2$ or superoxide radical anion $O_2^{\bullet -}$ [30] [41] [58] [59] [63]. According to the boundary orbital theory, only the interactions between the HOMO of the dye and the LUMO of the oxidant are considered [39]. The probability of a reaction is represented by the value of the superdelocalisation coefficient (S_r^E or S_r^N) on the appropriate nitrogen or carbon atom.

For our research, we used the AM1 and PM3 quantum-chemical calculation methods. The AM1 method is an enhanced MNDO method and uses the same input data. These are the most accurate methods used in many different calculations. Its advantages include correct mapping of interactions using hydrogen bonds, good prediction of activation energy barriers and molecular formation heat with an error of up to 40% less than in the MNDO method. Changing some of the theoretical assumptions (functions describing the repulsion between atomic cores) and assigning new parameters to them improves the efficiency of the AM1 and PM3 methods.

The main problems are the incorrect length of the oxygen-phosphorus bonds, as the nitro derivatives have excessive positive energies and the bonds in peroxides are too short. Therefore, in many cases, the PM3 method is used, which is an improved version of AM1.

The PM3 method is a reparametrised version of AM1, based on neglecting the diatom overlap approximation (NDDO). The PM3 method differs from AM1 only in the values of input parameters for calculations. The parameters in the PM3 method are derived from a wide variety of experimental data, and their comparison with the calculated properties particles using computer methods. Typical non-bonding interactions are weaker than those resulting from the calculations of the AM1 method. The PM3 is mainly used for the calculation of organic molecules, it also has parameters for the calculation of many major groups of elements. It is also used to test transition metal compounds, such as Ti, Mn, Fe, Co, Ni, Cu, Zr, Mo, Rh, Pd, Hf, Ta and W.

2. Methodology

The molecular structures of all derivatives were fully optimised using semi-empirical AM1 and PM3 quantum chemical computation methods with full optimization of all bond lengths, angles, and torsion angles (HyperChem v.8.0.6, HyperCube Inc.). After obtaining structures optimised in the ground state by the MM+ molecular mechanics method, the geometry of the molecule was completely

optimised without any geometrical constraints (RMS gradient 0.01 kcal/Amol), molecular dynamics (MDs; run time 1 ps, step size 0.001 ps, simulation temperature 300 K) and the AM1 or PM3 methods. Finally, the Hartree-Fock Hamiltonian (UMF) was used to calculate the CI configuration interaction in the gas phase at 25˚C. MD and AM1 or PM3 calculations were performed 3 to 5 times until a constant lowest standard enthalpy of formation H_f (kcal mol^{-1}) was obtained (convergence limit 0.01 kcal/mol). Singlet ground state energies were refined by using multielectron configuration interactions that analysed all combinations of six electrons in the three highest occupied molecular orbitals (HOMO) and the three lowest unoccupied molecular orbitals (LUMO).

3. Results and Discussion

All dyes were subjected to MO calculations using the AM1 method [64] [65] and compared with calculations made by PM3 methods [33] [66]. The calculations were conducted under the assumption that the molecules are in a vacuum and did not consider interactions of the dyes with fibers or with the products of their photochemical decomposition.

In the calculations of dye properties, they are not associated, and their photochemical degradation is much faster than the physical disintegration of the fiber [40] [59]. Hence, the latter factor may not be taken into account when interpreting the results [53] [60].

The calculations show the electron densities on individual atoms in the ground HOMO and the excited LUMO energy level of the dye. Frontier's molecular orbital theory suggests that the high electron density area in the dye HOMO is the site of singlet oxygen $^1O_2$ electrophilic attack. The area of high electron density in the LUMO is the location where the nucleophilic attack by the anion radical $O_2^{\bullet -}$ takes place [61] [67]. It is assumed that the attack of the electrophilic factor occurs when the energy difference ΔE between the singlet oxygen LUMO and the HOMO of the dye is less than 6 eV [39] [60].

The mechanism of the oxidation reaction with C=C singlet oxygen bonds using the MINDO/3 method is described by Dewar and Thiele [68], and other authors [40] [67] [69].

In our study, we performed calculations of the electron density of the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO of the dye.

Superdelocalisability ($S_r^{E(N)}$) describes the relative propensity of compounds to electrophilic and nucleophilic reactions with oxygen:

$$S_r^{E(N)} = \frac{f_r^{E(N)}}{E_{\text{HOMO(LUMO)}}}(-a) \tag{1}$$

where ($f_r^{E(N)}$) is a measure of the electron density in the ground/excited state on the r-atom and a is multiplied to make this value positive (−1 eV), this allows to compare the reactivity of the corresponding atoms in various molecules [60]

[69]-[71].

In our analysis, we made the following assumptions [40]:

- the place of electrophilic reaction (E) with singlet oxygen $^1O_2$ is the atom with the highest i.
- if the attack is to be effective, the energy difference of the HOMO state for factor E or N should be less than ≈ 6 eV (similarly as for azo dyes).
- and (superdelocalisation) determines the potential tendency to electrophilic and nucleophilic reactions, but these values cannot be correlated with light fastness.

The larger these values are, the greater the likelihood of a reaction at carbon C using one of the active oxygen species. The results of the electrophilic (S_r^E) and nucleophilic (S_r^N) attack location calculations are presented in the table and in the figures.

The tested monoazo dyes, derivatives of 5-(4-X-phenylazo)-3-cyano-1-(H or C_2H_5)-6-hydroxy-4-methyl-2-pyridone, are obtained in a conventional coupling reaction. Studies of their IR and UV-Vis spectra indicate that they usually occur in the hydrazone form, although in solvents other than DMSO they may also occur in the form of the tautomeric equilibrium [AZO—HYD] [31] [42] [43].

It is possible to predict the most probable tautomers of the studied dyes (azo-hydrazone or lactam-lactim) by means of quantum-chemical calculations and analysing changes in the energy of their formation (enthalpy) [72]-[78].

Using the *ab initio* method of quantum-chemical calculations, greater stability of the lactam form than of the lactim form was predicted [79]-[81]. For example, crystalline 5-amino-3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridone derivatives have been found to exist as a hydrazone, while in various solvents as an equilibrium [AZO—HYD].

Using UV-Visible spectrophotometric methods, changes in absorption and their intensity (ε_{max}) are observed in the ranges assigned to individual AZO and/or HYD tautomers. However, absorption bands result from the overlapping of partial bands assigned to all AZO or HYD tautomers. The above situation results from the fact that the bands (AZO, HYD) have very similar values of their absorption maxima λ_{max} [82].

AZO1, AZO2 dyes are lactam tautomers of the AZO3 lactim form, HYD1, HYD2 dyes are lactim tautomers, and HYD3 are lactam tautomers. According to the literature [79], the lactim form with an aromatic structure (e.g. AZO3) should be the most stable (**Figure 1**).

The results of the calculation enthalpy in the formation [AZO, HYD] tautomers and reactivity coefficient SE for the [ene] reaction are presented in **Tables 1(a)-6(b)** and a graphical presentation of changes in **Figure 2**. The results of the calculation for the most propable location of the electrophilic and nucleophilic reaction are presented in **Tables 7(a)-9(b)** and their exemplary graphic presentation in **Figure 3** and **Figure 4**. The diameters of the circles are proportional to the superdelocalisation value. For our research, we chose derivatives with the

largest possible difference in the σ_p-Hammett constants of the substituents (σ_p = −0.17 (Me), σ_p = −0.00(H), and σ_p = +0.78 (NO_2) [1].

4. Tautomerism [AZO-HYD]

4.1. 5-(4-Nitrophenylazo)-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone (Table 1(a) and Table 1(b))

[AM1 method] NH_NO2 derivatives exist in the form of the tautomeric equilibrium [AZO—HYD] typical for 2-pyridone derivatives (**Figure 1**). At the same time, they may occur in the form of a tautomeric lactam-lactim equilibrium.

The HYD3 tautomer have the lowest heat of formation (H = 48.339 kcal/mol) and the highest probability of formation. The remaining tautomers should be formed in the order (ΔH kcal/mol, **Table 1(a)**):

HYD3 < AZO1(+5.456) < AZO2(+6.506) < AZO3(+11.036) < HYD2(+16.632) < HYD1(+20.920)

Table 1(a). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-(4-nitrophenylazo)-3-cyano-(1-H)-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the AM1 method for the reaction [ene].

	NH_NO2					
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3
ΔE[kcal/mol]	53.795	54.845	59.375	69.259	64.971	48.339
C1/C2	0.0202		0.0205			
C1/C3	0.0205	0.214		0.202	0.0191	0.0200
C3/C4			0.0207	0.203	0.0206	0.0203

[**PM3 method**]. In the **PM3** method, the order is as follows (AZO1 27,709 kcal/mol; ΔH kcal/mol, **Table 1(b)**):

AZO1 < HYD3(+1.538) < AZO2(+2.020) < AZO3(+2.757) < HYD2(+13.913) < HYD1(+19.024)

Table 1(b). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-(4-nitrophenylazo)-3-cyano-(1-H)-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the PM3 method for the reaction [ene].

	NH_NO2					
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3
ΔE[kcal/mol]	27.709	29.729	30.466	46.733	41.622	29.247
C2/C6			0.0122			
C1/C3			0.0452			
C3/C4	0.0116	0.0111				
C5/C6(C4)		0.0139 (0.0113)		0.0187 (0.0219)	0.0192 (0.0216)	0.0214 (0.0189)

The NEt derivatives are formed in the following order (H, ΔH kcal/mol):

[**AM1**, Table 2(a)] HYD3(49.714) < AZO1(+5.363) < AZO2(+6.317)

[**PM3**, Table 2(b)] AZO1(20.042) < HYD3(+8.737) < AZO2(+9.737)

Table 2(a). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-(4-nitrophenylazo)-3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the AM1 method for the reaction [ene].

	NEt_NO2		
	AZO1	AZO2	HYD3
ΔE [kcal/mol]	55.077	56.031	49.714
C1/C2(C3)	0.0210	0.0217	(0.0203)
C3/C4	0.0213	0.0222	0.206
N8/C9		0.0263	
C15/C16	0.0291	0.0297	0.272

Table 2(b). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-(4-nitrophenylazo)-3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the PM3 method for the reaction [ene].

	NEt_NO2		
	AZO1	AZO2	HYD3
ΔE [kcal/mol]	20.042	29.779	28.797
C1/C2(C3)	0.0445	(0.0478)	
C5/C6(C4)			0.0215 (0.0189)
C15/C16	0.0209	0.0260	0.0238

According to the AM1 method, in the NH derivative, the HYD3 tautomer is the most probable form, followed by the AZO1 tautomer, while the HYD1 tautomer is the least probable.

The PM3 method, however, indicates that the formation of the AZO1 tautomer is the most probable, followed by HYD3. However, the energy differences between these tautomers allow to assume that the state of azo-hydrazone equilibrium with small energy changes should be taken into account. According to literature data, 2-pyridone derivatives should occur mainly in the form of a hydrazone tautomer, however, these considerations do not concern the possibility of occurrence of these derivatives in the form of imido-iminol tautomers.

Spectrophotometric data do not confirm theoretical research. More precise conclusions will be possible using the method of deconvolution bands absorption into their components, described by Antonov and co-workers [82]. This method also allows to identify hidden absorption bands that can be attributed to different tautomers and to determine their percentages and equilibrium constants K_T in the mixture.

NEt derivatives according to AM1 methods (Table 2(a)) occur mainly in the

form of the HYD3 tautomer, the least in the form of AZO2. In the PM3 method (Table 2(b)), the most stable form is the tautomer AZO1, the least stable and probable is AZO2.

4.2. 5-Phenylazo-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone (Table 3(a) and Table 3(b))

[**AM1 method**] These derivatives exist in the form of the HYD3 tautomer, its enthalpy of formation is 43,070 kcal/mol.

Table 3(a). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-phenylazo-3-cyano-1-H-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the AM1 method for the reaction [ene].

	NH_H					
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3
ΔE[kcal/mol]	48.636	50.620	54.441	64.020	59.842	43.070
C1/C3	0.0273	0.0285	0.0266	0.0269	0.0271	0.0267
C2/C6	0.0270	0.0277	0.0261	0.0290	0.0285	0.0284

Table 3(b). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-phenylazo-3-cyano-1-H-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the PM3 method for the reaction [ene].

	NH_H					
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3
ΔE[kcal/mol]	32.842	38.305	36.572	47.975	47.941	33.006
C2/C6			0.0203			
C1/C3(C2)	(0.0211)	0.0224	0.0214	0.0202	0.0202	(0.0201)
C3/C4	0.0204					
C5/C6(C4)		0.0186	0.0185	0.0242 (0.0208)	0.0275 (0.0248)	0.0218 (0.0244)

The other forms are less durable and the energy differences are (ΔH [kcal/mol], Table 3(a)):

HYD3 < AZO1(+5.566) < AZO2(+7.550) < AZO3(+11.371) < HYD2(+16.772) < HYD1(+20.950)

and in the **PM3** method, the order is as follows (AZO1 H = 32.842kcal/mol; ΔH kcal/mol, Table 3(b)):

AZO1 < HYD3(+0.164) < AZO3(+3.730) < AZO2(+5.463) < HYD2(+15.099) ≤ HYD1(+15.133)

In this derivative (**PM3** method) a small energy difference between the HYD2 and HYD1 tautomers is noticeable, about 0.2%.

NEt derivatives are probably formed in the following order (H, ΔH kcal/mol):

[**AM1**, Table 4(a)] HYD3(44.668) < AZO1(+5.492) < AZO2(+10.139)

Table 4(a). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-phenylazo-3-cyano-1-ethyl-6-hydroxy-4-methyl-2 pyridone derivatives calculated by the AM1 method for the reaction [ene].

	NEt_H		
	AZO1	AZO2	HYD3
ΔE [kcal/mol]	50.160	54.807	44.668
C1/C2(C3)	0.0276 (0.0278)	(0.0290)	0.0270
C2/C6	0.0275	0.0281	0.0266
C3/C4	0.0258		0.0287
C15/C16	0.0302	0.0306	

[**PM3**, **Table 4(b)**] HYD3(35.363) < AZO1(+0.254) < AZO2(+1.924)

Table 4(b). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-phenylazo-3-cyano-1-ethyl-6-hydroxy-4-methyl-2 pyridone derivatives calculated by the PM3 method for the reaction [ene].

	NEt_H		
	AZO1	AZO2	HYD3
	AZO1	AZO2	HYD3
ΔE [kcal/mol]	35.617	37.287	35.363
C1/C2(C3)	0.0217	(0.0226)	0.0201
C2/C6		0.0210	0.0193
C3/C4	0.0218		
C5/C6(C4)	(0.0193)	0.0180	(0.0265)
C15/C16	0.0271		0.0248

The HYD3 tautomer should form first, followed by the AZO1. However, the energy difference between these tautomers (PM3) is very small and amounts to only 0.254 kcal/mol.

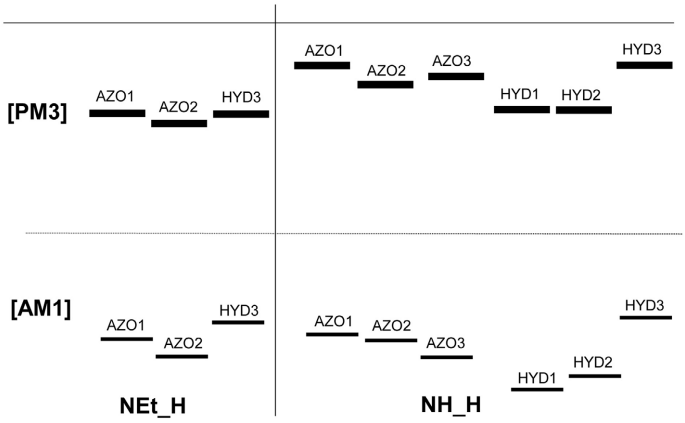

Figure 2. Graphical presentation of changes in the formation enthalpy for [AZO, HYD] tautomers of selected [NEt or NH] derivatives of 5-phenylazo-3-cyano-6-hydroxy-4-methyl-2-pyridone calculated using the AM1 and PM3 methods (see **Table 3(a)** and **Table 3(b)**, **Table 4(a)** and **Table 4(b)**).

[**PM3 method**]. Pyridone dyes containing the NH group occur in the forms AZO1 and HYD3. They are least likely to occur in the form HYD1 (Figure 2, Table 3(b)). This feature is confirmed by their enthalpies of formation and can be ordered as follows ($\Delta H = H_{HYD3} - H_{taut}$, where H_{taut}—energy of any tautomer, [kcal/mol]).

AZO1 > HYD3(+0.164) > AZO3(+3.730) > AZO2(+5.463) > HYD2(+15.099) ≈ HYD1(+15.134)

For NEt derivatives, the enthalpy differences in ΔH [kcal/mol] are smaller and are as follows (Table 4(b)):

AZO1 > HYD3(+0.394) > AZO2(+1.670)

In these derivatives, the dyes should exist mainly in the azo-lactam form, *i.e.* in the AZO1 or hydrazone HYD3. This is indicated by the very small energy difference between the tautomers.

In the phenylazo derivative (X=H) in the PM3 method, the differences in the enthalpy of formation of AZO1 and HYD3 isomers, both for NH and NEt derivatives, are very small and amount to 0.49% and 0.71%, respectively. These calculations allow us make conclusions about the ease of transition from one tautomeric form to another and the stabilisation of the equilibrium, whose state depends, for example, on external factors. As a result, the dye may change its shape and physicochemical properties, as well as its color or shade, e.g. depending on the conditions of thermal treatment.

4.3. 5-(4-Methylphenylazo)-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone (Table 5(a) and Table 5(b))

[**AM1 method**] The most likely tautomeric form is HYD3 (NH_H), with enthalpy of formation −35.245 kcal/mol. Other forms are less fast and can be ordered according to increasing energy (ΔH [kcal/mol], Table 5(a)):

HYD3 > AZO1(+5496) > AZO2(+7533) > AZO3(+15,507) > HYD2(+16,768) > HYD1(+20,954)

Table 5(a). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-(4-methylphenylazo)-3-cyano-1-H-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the AM1 method for the reaction [ene].

	NH_H					
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3
ΔE[kcal/mol]	40.741	42.778	50.752	56.199	52.013	35.245
C3/C4	0.0270	0.0249	0.0241	0.0263	0.0268	0.0265
C2/C6	0.0253	0.0277	0.0262	0.0291	0.0286	0.0285

[**PM3 method**] In this method, the dyes are arranged in the following series (the most probable is the AZO1 tautomer with H = 25,690 kcal/mol (ΔH [kcal/mol], Table 5(b)):

AZO1 > HYD3(+1.661) > AZO2(+3.112) > AZO3(+3.311) > HYD2(+13.261) > HYD1(+18.356)

Table 5(b). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E of 5-(4-methylphenylazo)-3-cyano-1-H-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the PM3 method for the reaction [ene].

	NH_H					
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3
ΔE[kcal/mol]	25.690	28.802	29.001	44.046	38.951	27.351
C2/C6						0.0192
C1/C3(C2)		0.0200	0.0188	0.0173	(0.0168)	
C3/C4	0.0194			0.0192		0.0217
C5/C6(C4)	0.0176	0.0194	0.0188	0.0284	0.0255 (0.0283)	(0.0279)

NEt derivatives can exist only in the form of three tautomers, and are as follows (H kcal/mol and ΔH kcal/mol):

[**AM1**, **Table 9(a)**] HYD3(36.857) < AZO1(+5.5452) < AZO2(+7.094)

Table 6(a). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E 5-(4-methylphenyloazo)-3-cyano-1-ethyl-6-hydroxy-4-methyl-2 pyridone derivatives calculated by the AM1 method for the reaction [ene].

	NEt_H		
	AZO1	AZO2	HYD3
ΔE [kcal/mol]	42.309	43.951	36.857
C2/C6	0.0259	0.0255	0.0287
C3/C4	0.0274	0.0280	0.0267
C15/C16	0.0304	0.0310	0.0291

[**PM3**, **Table 5(b)**] AZO1(25.166) < HYD3(+1.125) < AZO2(+3.441)

Table 6(b). Enthalpy (energy) of formation ΔE [kcal/mol] and reactivity coefficients S^E 5-(4-methylphenyloazo)-3-cyano-1-ethyl-6-hydroxy-4-methyl-2 pyridone derivatives calculated by the PM3 method for the reaction [ene].

	NEt_H		
	AZO1	AZO2	HYD3
ΔE [kcal/mol]	25.166	28.607	26.291
C1/C2(C3)	0.0189	(0.0201)	
C2/C6	0.0199	0.0209	0.0196
C3/C4	0.0207		
C5/C6(C4)			(0.0281)
C15/C16	0.0270	0.0274	0.0253

Calculations reveal that the dyes exist mainly as HYD3 (AM1) or AZO1 (PM3) tautomers. It can be assumed that these dyes exist in equilibrium of azo-hydrazone tautomeric forms, their proportions can change with a slight change in the energy of the system. The HYD1 tautomer is the least probable, both in the calculations made by AM1 and PM3 methods.

In the NEt derivatives, there are similar dependencies and tautomeric equilibrium between [HYD3 ⇆ AZO1], the least probable is AZO2 tautomer.

Derivatives containing the *p*–CH_3 group occur mainly in the azo-lactam form AZO1 and the lactam-hydrazone form HYD3 (Table 6(a) and Table 6(b)).

5. Electrophilic Photooxidation $^1O_2$ (S^E)

5.1. 5-(4-Nitrophenylazo)-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone

[**AM1 method**] Values calculated by AM1 method show, first of all, photooxidation reactions on the N13 nitrogen atom. Further order is as follows (tautomer, S^E, Table 7(a) and Figure 3):

HYD3(0.0370) > HYD2(0.0322) > AZO1(0.0304) > > AZO2(0.0303) > HYD1(0.0300) > AZO3(0.0254)

Table 7(a). Reactivity coefficients $S^{(E/N)}$ of 5-(4-nitrophenylazo)-3-cyano-(1-H or ethyl)-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the AM1 method in the electrophilic and nucleophilic oxidation reaction.

	AM1						AM1		
	NH_NO2						NEt_NO2		
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3	AZO1	AZO2	HYD3
C1	0.0135	0.0139	0.0128	0.0160	0.0158	0.0156	0.0137	0.0131	0.0159
C4	0.0124	0.0119	0.0134	0.0161	0.0160	0.0159	0.0144	0.0140	0.0162
C6	0.0142	0.0142	0.0107	0.0190	0.0183	0.0182	0.0125	0.0102	0.0186
C9	0.0292	0.0219	0.0173	0.0161	0.0249	0.0203	0.0300	0.0220	0.0199
N7	0.0181			0.0218	0.0206	0.0211	0.0189		0.0215
C11	0.0177	0.0247	0.0201	0.0121	0.0103	0.0104	0.0185	0.0258	
C16(Et)							0.0248	0.0253	0.0240
C(CH3)	0.0211	0.0216	0.0209	0.0206	0.0213	0.0209	0.0213	0.0217	0.0369
N13	0.0304	0.0303	0.0254	0.0300	0.0322	0.0370	0.0255	0.0253	0.0323

Nucleophilic reaction.

C12	0.1676	0.0974	0.0998	0.1273	0.0850	0.1507	0.1691	0.0955	0.1570
C14	0.0652	0.1993	0.0964	0.0585	0.1172	0.1384	0.0673	0.1913	0.1446

Nitro derivatives should then oxidise on the N7(H) atom of the HYD form or

C9 of the AZO form. The reaction should therefore proceed through an N-oxide or nitroso group. The highest reactivity is characteristic of the heterocyclic ring, the reactivity of carbon atoms in the phenylazo residue is up to 2 times lower than the reactivity of the N13 atom in the heterocycle ring.

The NEt derivatives should react in the following order (atom, S^E, Table 7(a)):

HYD3(C(CH3), 0.0369) > AZO1(C9, 0.0300) > AZO2(C11, 0.0258)

The reaction products will therefore depend on the tautomeric form in which the dye will be present. As in the NH derivative, nitrogen and carbon atoms in the heterocyclic ring are characterised by higher reactivity.

[**PM3 method**] Calculations made by the PM3 method indicate that the C1 atom of the phenyl ring is the most reactive, followed by the C9 atom of the heterocyclic ring (S^N(C1), S^N(C1)/S^N(C9)) (Table 7(b) and Figure 3):

HYD1(0.0475, 2.04) > HYD2(0.0471, 1.42) > HYD3(0.0468, 1.58) > AZO2(0.0463, 1.66) > AZO1(0.0452) > AZO3(0.0443, 1.97)

Table 7(b). Reactivity coefficients $S^{(E/H)}$ of 5-(4-nitrophenylazo)-3-cyano-1-(H or ethyl)-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the PM3 method in the electrophilic and nucleophilic oxidation reaction.

	PM3						PM3		
	NH_NO2						NEt_NO2		
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3	AZO1	AZO2	HYD3
C1	0.0452	0.0463	0.0443	0.0475	0.0471	0.0468	0.0436	0.0463	0.0473
C4	0.0112	0.0100		0.0171	0.0160	0.0136			0.0139
C6	0.0127	0.0126	0.0119	0.0138	0.0136	0.0161	0.0111	0.0122	0.0164
C9	0.0352	0.0278	0.0225	0.0233	0.0331	0.0296	0.0387	0.0286	0.0295
N7	0.0142						0.0163		
C11	0.0155	0.0215	0.0168				0.0168	0.0231	0.0103
C16(Et)							0.0139	0.0139	0.0138
C(CH3)	0.0107	0.0110	0.0105				0.0102	0.0123	0.0104
N13	0.0170		0.0188	0.0241	0.0275			0.0167	

Nucleophilic reaction.

C12	0.0994		0.1003	0.1169	0.0736	0.1021	0.1236		0.1094
N13(N7)	0.1294	0.1073		(0.2253)	(0.2238)	(0.2331)	0.0837	0.1016	(0.2405)
C14		0.1334	0.0960	0.0456	0.1172	0.0920		0.1327	0.1006

The C1 atom owes its high reactivity to the presence of a strong E_A substituent, which is the nitro group. NEt derivatives (S^N(C1), S_N(C1)/S^N(C9)) react similarly (Table 7(b) and Figure 3):

HYD3(0.0473, 1.60) > AZO2(0.0463) > AZO1(0.0436, 1.13)

The C1 atom owes its high reactivity to the presence of a strong E_A substituent, which is the nitro group. NEt derivatives (S^N(C1), S_N(C1)/S^N(C9)) react similarly (tab.7b):

HYD3(0.0473,1.60) > AZO2(0.0463) > AZO1(0.0436,1.13)

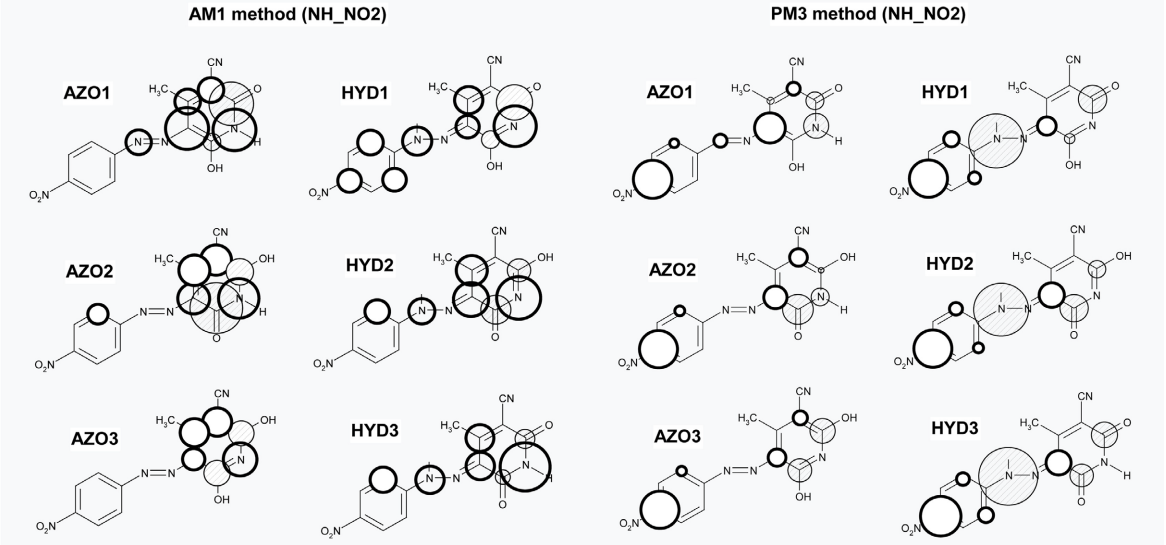

Figure 3. Example of a graphical representation of superdelocalisability for electrophilic S^E (○)and nucleophilic photooxidation S^N (⊘) of [AZO—HYD] tautomers of 5-(4-nitrophenylazo)-3-cyano-1-H-6-hydroxy-4-methyl-2-pyridone dyes as calculated by the AM1 and PM3 methods (circle diameters are proportional to values of the superdelocalisability coefficients) (**Table 1(a)** and **Table 1(b)**; **Table 7(a)** and **Table 7(b)**).

The NEt derivatives should react with $^1O_2$ in a similar manner. The most reactive position is on the C1 carbon atom in the aromatic ring (**Table 7(b)**). The next reaction should take place on the C9 atom (S^N(C1), S^N(C1)/S^N(C9)):

HYD3(0.047, 1.605) > AZO2(0.046, 1.619) > AZO1(0.044, 1.128)

The reaction should lead to heterolytic degradation of bonds in the aromatic ring of diazo compounds. In *p*-NO_2 derivatives, photochemical decomposition is higher than in derivatives with E_D groups. In the diazo compounds, the C1 carbon atom is the place where a dye molecule, first, undergoes photochemical oxidation of $^1O_2$ (S_E). The reactivity of the C9 atom is also high and comparable to reactivity of the other dyes (*p*-CH_3, *p*-H), in which the photooxidation takes place on the C9 carbon atom in the 2-pyridone ring (**Table 2(a)** and **Table 2(b)**, **Table 3(a)** and **Table 3(b)**). Only the PM3 method indicates high reactivity of nitro derivatives on the C1 atom. This conclusion is consistent with the results of the research on azo dyes, *i.e.* it proves the low fastness to oxidation of the phenyl ring [76] [83].

5.2. 5-Phenylazo-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone

In an electrophilic reaction, they undergo photooxidation on the C9 carbon atom

of the heterocyclic ring.

[**AM1 method**] Calculations made by AM1 method indicate that electrophilic oxidation of $^1O_2$ should first occur on the N13 nitrogen atom of the heterocyclic ring. The reactivity can be ranked as follows (S^E, Table 8(a) and Figure 4):

HYD3(0.0394) > HYD2(0.0346) > HYD1(0.0332) > AZO1(0.0321) > AZO2(0.0321) > AZO3(0.0272)

Table 8(a). Reactivity coefficients $S^{(E/N)}$ of 5-phenylazo-3-cyano-1-(H or ethyl)-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the AM1 method in the electrophilic and nucleophilic oxidation reaction.

	AM1						AM1		
	NH_H						NEt_H		
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3	AZO1	AZO2	HYD3
C1				0.0150	0.0148	0.0147	0.0129	0.0131	0.0150
C2	0.0145						0.0147	0.0156	
C3	0.0147	0.0158	0.0146				0.0150	0.0160	
C4				0.0145		0.0143			0.0171
C6	0.0125			0.0176	0.0168	0.0169			
C9	0.0298	0.0207	0.0248	0.0211	0.0302	0.0256	0.0308	0.0214	0.0253
N7	0.0175		0.0136	0.0211	0.0195	0.0203	0.0181		0.0208
C11	0.0194	0.0253	0.0151				0.0201	0.0263	0.0133
C16(Et)							0.0259	0.0264	0.0254
C(CH3)	0.0220	0.0223	0.0213	0.0219	0.0226	0.0222	0.0222	0.0225	0.0222
N13	0.0321	0.0321	0.0272	0.0332	0.0346	0.0394	0.0270	0.0269	0.0343

Nucleophilic reaction.

C12	0.2703	0.1391	0.1055	0.1648	0.1068	0.2010	0.2903	0.1468	0.2131
C14	0.0877	0.3227	0.1173	0.0710	0.1508	0.1832	0.0926	0.3333	0.1945

Next, the reaction should take place on the C9 carbon atom in the heterocyclic ring (S^N(N13)/S^N(C9)):

HYD3(1.54) > HYD2(1.15) > HYD1(1.57) > AZO1(1.08) > AZO2(1.55) > AZO3(1.10)

The NEt derivatives react similarly, and the corresponding relationships are as follows (S^N(N13), S^N(N13)/S^N(C9)) (Table 8(a)):

HYD3(0.0343, 1.36) > AZO1(0.0270, 0.88) > AZO2(0.0269, 1.02)

[**PM3 method**] The most reactive is the N13 (AZO3, HYD1) or C9 (AZO1, AZO2, HYD2, HYD3) atom of the heterocyclic ring. The reactivity of these atoms can be arranged as follows (atom, S^N, Table 8(b) and Figure 4):

HYD2(C9.0.0392) > HYD3(C9.0.0358) > AZO1(C9.0.0352) > HYD1(N13.0.0288) > AZO3(N13.0.0267) > AZO2(C9.0.0264)

Table 8(b). Reactivity coefficients S^E of 5-phenylazo-3-cyano-1-(H or ethyl)-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the PM3 method in the electrophilic and nucleophilic oxidation reaction.

	PM3						PM3		
	NH_H						NEt_H		
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3	AZO1	AZO2	HYD3
C1				0.0111	0.0105	0.0108			
C2	0.0118						0.0118		
C3		0.0130	0.0124					0.0131	
C4						0.0127			0.0126
C6					0.0151	0.0117			0.0139
C9				0.0135	0.0125				
N7	0.0352	0.0264	0.0214	0.0243	0.0392	0.0358	0.0351	0.0270	0.0357
C11	0.0114								
C16(Et)	0.0169	0.0225	0.0110	0.0115	0.0119	0.0127	0.0182	0.0233	0.0129
C(CH3)							0.0144	0.0148	0.0146
N13	0.0112	0.0122	0.0108	0.0101	0.0115	0.0106	0.0125	0.0121	0.0110

Nucleophilic reaction.

C12	0.2004		0.1902	0.1440	0.0929	0.1498	0.1773		0.1531
N13(N7)	0.1151	0.1322		(0.1106)	(0.2762)	(0.2628)	0.2093	0.1451	(0.3119)
C14	0.1123	0.1805	0.1869	0.0439	0.1503	0.1263		0.2115	0.1351

NEt derivatives should react on the C9 carbon atom and their reactivity is as follows (**Table 8(a)** and **Table 8(b)**):

HYD3(0.0357) > AZO1(0.0351) > AZO2(0.0270)

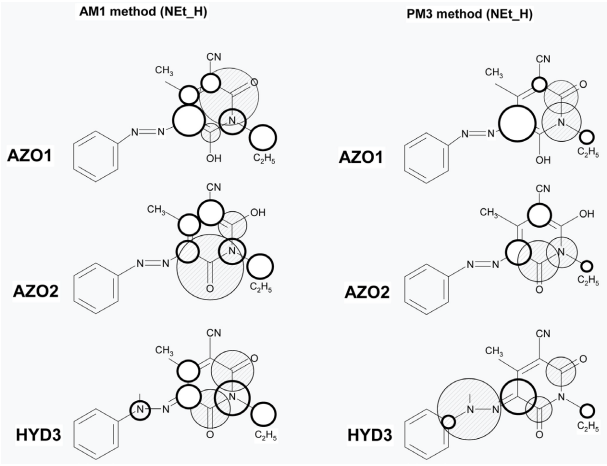

Figure 4. Graphical representation of the superdelocalisation coefficient for the electrophilic S^E (○) and nucleophilic photooxidation S^N (⊘) of [AZO—HYD] tautomers of the 5-phenylazo-3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridone dyes calculated by AM1 and PM3 methods (circle diameters are proportional to the values of the superdelocalisability coefficients) (**Table 8(a)** and **Table 8(b)**).

5.3. 5-(4-Methylphenylazo)-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone

[**AM1 method**] In the N-H derivative, in the electrophilic oxidation reaction of $^1O_2$, the most reactive is the N13 nitrogen atoms on the heterocyclic ring in the following order (S^E, Table 9(a)):

HYD3(0.0399) > HYD2(0.0351) > HYD1(0.0337) > AZO1(0.0324) = AZO2(0.0324) > AZO3(0.0197)

In the next bond, the reaction should take place on the C9 atom in the pyridone ring:

HYD2(0.0308) > AZO1(0.0299) > HYD3(0.0262) > AZO2(0.0255) > AZO3(0.0249) > HYD1(C(CH3), 0.0221)

Table 9(a). Reactivity coefficients $S^{(E/N)}$ of 5-(4-methyphenylazo)-3-cyjano-1-(H or ethyl)-6-hydroxy-4-methyl-2 pyridone derivatives calculated by the AM1 method in the electrophilic and nucleophilic oxidation reaction.

	AM1						AM1		
	NH_CH3						NEt_CH3		
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3	AZO1	AZO2	HYD3
C2	0.0152						0.0154		0.0121
C3	0.0150	0.0162	0.0150				0.0150	0.0161	
C4				0.0140					0.0140
C6			0.0113	0.0171					0.0167
C9	0.0299	0.0206	0.0249	0.0216	0.0308	0.0262	0.0309	0.0213	0.0259
N7	0.0174		0.0132	0.0210	0.0194	0.0203	0.0180		0.0207
C11	0.0196	0.0255	0.0221	0.0151			0.0203	0.0264	0.0136
C16(Et)							0.0261	0.0267	0.0257
C(CH3)	0.0222	0.0224	0.0216	0.0221	0.0229	0.0225	0.0224	0.0226	0.0225
PhC(CH3)	0.0206	0.0209	0.0201	0.0202	0.0204	0.0202	0.0208	0.0211	0.0203
N13	0.0324	0.0324	0.0197	0.0337	0.0351	0.0399	0.0272	0.0270	0.0348
Nucleophilic reaction									
C12	0.2782	0.1454	0.1106	0.1680	0.1099	0.2053	0.3013	0.1592	0.2175
C14	0.1081	0.3297	0.1170	0.0726	0.1537	0.1866	0.1151	0.3721	0.1986

These calculations show that the pyridone phenyl ring is responsible for the photooxidation fastness in the electrophilic reaction. The reactivity of C1 ÷ C6 carbon atoms in the phenylazo residue is much lower, more than twice as low, than that of the atoms in the heterocycle.

NEt derivatives react similarly to NH, mainly on the N13 nitrogen atom, only

in the AZO1 tautomer the reaction should first take place on the C9 carbon atom (atom, S^E, Table 9(a)):

HYD3(N13, 0.0348) > AZO1(C9, 0.0309) > AZO2(N13, 0.0270)

The calculations show that the photochemical stabilities of 2-pyridone derivatives depend on the type of tautomer in which they occur. The general relationship, however, is the conclusion that the electrophilic reaction occurs first in the phenyl ring, whose photooxidation fastness may be even 2.87 times lower than that of the atoms in the pyridone ring (e.g. NEt, HYD3, N13:C2 = 2.87).

[**PM3 method**] Calculations made by the PM3 method indicate a different course of the reaction. In this method, the C9 carbon atom of the heterocyclic ring is the most reactive followed by the reaction on the C11 atom to which a strong electron withdrawing substituent (E_A) cyano group -CN is attached. The reactivity of these derivatives can be as follows (S^E[C9], S^E[C9]/S^E[C11], Table 9(b)):

HYD2(0.0399, 3.24) > HYD3(0.0365, 2.68) > AZO1(0.0352, 2.06) > HYD1(0.0301, 2.16) > AZO2(0.0263, 1.18) > AZO3(0.0215, 1.18)

and for NEt derivatives (as above) (Table 9(b)):

HYD3(0.0365, 2.63) > AZO1(0.0364, 2.03) > AZO2(0.0269, 1.16).

HYD3(N7.0.3080) > AZO2(C14.0.2124) > AZO1(N7.0.1899)

Table 9(b). Reactivity coefficients $S^{(E/N)}$ of 5-(4-methylphenylazo)-3-cyano-1-(H or ethyl)-6-hydroxy-4-methyl-2-pyridone derivatives calculated by the PM3 method in the electrophilic and nucleophilic reaction.

	PM3						PM3		
	NH_CH3						NEt_CH3		
	AZO1	AZO2	AZO3	HYD1	HYD2	HYD3	AZO1	AZO2	HYD3
C2	0.0121	0.0133	0.0127				0.0127		
C3	0.0123	0.0140	0.0134					0.0137	
C4									0.0122
C6(C5)				(0.0156)	(0.0166)	(0.0161)			(0.0159)
C9	0.0352	0.0263	0.0215	0.0301	0.0399	0.0365	0.0364	0.0269	0.0365
N7							0.0115		
C11	0.0171	0.0223	0.0181	0.0139	0.0123	0.0136	0.0179	0.0232	0.0139
C16(Et)							0.0145	0.0147	0.0147
C(CH3)					0.0116	0.0113			
N13			0.0203						

Nucleophilic reaction.

C12	0.1525		0.1322	0.1548	0.0955	0.1376	0.1675		0.1484
N13(N7)	0.1844	0.1436		(0.2832)	(0.2820)	(0.2957)	0.1899	0.1401	(0.3080)
C14		0.1895	0.1385	0.0546	0.1535	0.1207		0.2124	0.1325

The performed calculations indicate a different likely reaction mechanism in the AM1 and PM3 methods. In the former, the reaction products may be nitroso or nitro derivatives, then ketones or acids. In the PM3 method, the reaction should take place in the heterocyclic ring on the C9 atom through peroxide structures. There is no high reactivity of the nitrogen in the azo or hydrazone bond. Only in the nucleophilic oxidation reaction, the reaction can take place as a result of the reaction of nitrogen N7(H) or N13, especially in the hydrazone form of the dye.

In the analysis of the reactivity of molecules to electrophilic $^1O_2$ oxidation, a high value of the superdelocalisabillity coefficient S^E was not observed on the adjacent atoms of non-ionised molecules, hence they can undergo photochemical decomposition only through an epoxidation mechanism.

6. Nucleophilic Photooxidation $O_2^{\bullet-}$ (S^N)

6.1. 5-(4-Nitrophenylazo)-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone

[**AM1 method**] In the nucleophilic photooxidation, the reaction should take place on the C12 or C14 atom. The NH derivatives should react in the following order (atom, S^N, Table 7(a)):

AZO2(C14, 0.1993) > AZO1(C12, 0.1676) > HYD3(C12, 0.1507) > HYD1(C12, 0.1273) > HYD2(C14, 0.1172) > AZO3(C12, 0.0998)

and for NEt (atom, S^N, Table 7(a)):

AZO2(C14, 0.1913) > AZO1(C12, 0.1691) > HYD3(C12, 0.1570)

i.e. the carbonyl carbon atom is most reactive.

[**PM3 method**] In the nucleophilic reaction, the hydrazone nitrogen atom N7(H) in the HYD1 ÷ HYD3 tautomers is characterised by high reactivity, the AZO tautomers react almost 1.8 - 2 times slower on the carbonyl atom C12 or C14. For the NH derivative, the reactivity of individual atoms can be arranged as follows (atom, S^N, Table 7(b)):

HYD3(N7, 0.2331) > HYD1(N7, 0.2253) > HYD2(N7, 0.2238) > AZO2(C14, 0.1334) > AZO1(N13, 0.1294) > AZO3(C12, 0.01003)

and for the derivative NEt (atom, S^N, Table 7(b)):

HYD3(N7, 0.2405) > AZO2(C14, 0.1327) > AZO1(C12, 0.1236)

The calculations performed using the AM1 and PM3 methods indicate different oxidation mechanisms. The AM1 method indicates that oxidation should take place in the heterocyclic ring on the N13 nitrogen atom, then on the C9 atom, while in the PM3 method, the reaction should take place first on the C1 atom of the phenyl ring, whose reactivity is even 2 times higher than that of the carbon C9 (e.g. HYD1).

6.2. 5-Phenylazo-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone

[**AM1 method**] In the $O_2^{\bullet-}$ nucleophilic reaction, the reaction should take place

at the C12 or C14 carbonyl atom (atom, S^N, Table 8(a)):

[NH] AZO2(C14, 0.3227) > AZO1(C12, 0.2703) > HYD3(C12, 0.2010) > HYD1(C12, 0.1648) > HYD2((C14, 0.1508) > AZO3(C14, 0.1173)

[NEt] AZO2(C14, 0.3303) > AZO1(C12, 0.2903) > HYD3(C14, 0.1945)

[**PM3 method**] In the nucleophilic reaction $O_2^{\bullet -}$ hydrazone derivatives react first on the N7(H) nitrogen atom (S^N, Table 8(b)):

HYD2(N7, 0.2762) > HYD3(N7, 0.2628) > AZO1(C12, 0.2004) > AZO3(C12, 0.1902) > AZO2(C14, 0.1805) > HYD1(C12, 0.1440)

That is, similarly to the previously discussed derivatives, the reaction should take place in a tautomeric form with a carbonyl carbon atom.

The NEt derivatives react as follows (atom, S^N, Table 8(b)):

HYD3(N7, 0.3119) > AZO2(C14, 0.2115) > AZO1(N13, 0.2093)

The PM3 method differs from AM1 in that it considers the probability of reaction at the N7 hydrazone nitrogen atom, whereas in the AM1 method, only C12 or C14 carbonyl carbon atoms are reactive.

6.3. 5-(4-Methylphenylazo)-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone

[**AM1 method**] The nucleophilic oxidation reaction of $O_2^{\bullet -}$ occurs exclusively on C12 or C14 atoms to which oxygen atoms -OH or =O are attached. The carbon atom in the C=O carbonyl group is characterised by the highest reactivity. The reactivity differences are significant and amount to (atom, S^N[C=O]/S^N[C-OH], Table 9(a)):

AZO1(C12, 2.57) > HYD1(C12, 2.31) > AZO2(C14, 2.27) > HYD2(C14, 1.39) > AZO3(C14, 1.06) > HYD3(C12, 1.10)

and for NEt derivatives (as above) (Table 9(a)):

AZO1(C12, 2.62) > AZO2(C14, 2.34) > HYD3(C12, 1.09)

If the C12 and C14 atoms are similar in nature and form C=O carbonyl groups, their reactivity is similar, differing only by about 6% - 9% (HYD3).

[**PM3 method**] In the nucleophilic photooxidation, the reaction should first take place on the hydrazone nitrogen atom N7(H). Reactivity on this atom is greater than on C12 or C14 (S^E[N7], S^N[N7]/S^N[C12 or C14], atom, Table 9(b)):

HYD3(0.2957, 2.15, C12) > HYD1(0.2832, 1.83, C12) > HYD2(0.2820, 1.84, C14)

In this reaction, the azo tautomers AZO1 ÷ AZO3 have low superdelocalisabilitie coefficients and the reaction should take place on the C14(AZO2, AZO3) or N13(AZO1) atom.

The NEt derivatives react as follows (atom, S^E, Table 9(b)):

HYD3(0.3080, N7) > AZO2(0.2124, C14) > AZO1(0.1899, N7)

7. [ene] Double Bond Reaction

For the studied tautomers, we calculated the reactivity coefficients of double

bonds in the electrophilic $^1O_2$ oxidation reaction. These reactions may compete with oxidation on the C or N atoms in the molecule. Their values were calculated according to Equation (1), where the electron density on the double bond is the result of the sum of the LUMO level charges of the neighboring atoms.

The analysis of the obtained results leads to the conclusion that the phenyl ring, mainly the C2=C6 or C3=C4 bond, is responsible for the light resistance.

7.1. 5-(4-Nitrophenylazo)-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone

In the AM1 method (Table 1(a), Table 2(a)), the most likely decay mechanism is on C1/C3 atoms in AZO2 (0.0214) tautomer, then C3=C4 in AZO3(0.0207) and HYD2(0.0206) and C1=C3 in AZO1(0.0205).

In the PM3 method (Table 1(a) and Table 1(b)) the C1=C3 bond in AZO3 is almost twice as reactive (0.0452) than the bond in HYD1(0.0219, C5=C6) and C5=C6 in HYD2(0.0216).

NEt derivatives, as in the cases of dyes discussed above, the ethyl substituent has the highest reactivity for electrophilic oxidation.

In the AM1 method, in the AZO2 tautomer it is 0.0297, in AZO1 it is 0.0291, while in the PM3 method it is 0.0260 in AZO2 and 0.0238 in HYD3.

Only in these derivatives, in the PM3 method, there is a probability that oxidation occurs on C5=C6(C4) atoms in the [**ene**] reaction The superdelocalisability coefficients on these bonds: C1=C2(C3) in the AZO2(0.0478) and AZO1(0.0445) tautomers are almost twice as high as in the Et substituent in NEt-2-pyridone.

7.2. 5-Phenylazo-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone

Calculations using the AM1 method (Table 3(a)) indicate that the most reactive bond in the [**ene**] reaction is the C2=C6 in the HYD1 tautomer (S^E = 0.0290) in HYD2 (S^E = 0.0285) and AZO2 (S^E = 0.0285, C1=C3).

However, calculations using the PM3 method (Table 3(b)) indicate that the [**ene**] reaction should take place on the C5=C6(C4) bond. The most likely reaction is in the tautomer HYD2(S^E = 0.0275, C5=C6) followed by HYD3 (S^E = 0.0244, C5=C4) and HYD1 (S^E = 0.0242, C5=C4).

The NEt isomer reacts first on the Et group (AZO2, 0.0306 [AM1]) and (AZO1, 0.0271 [PM3], Table 4(a) and Table 4(b)). Next, the reaction should take place in AZO1(0.0302, Et [AM1], Table 3(a)) and HYD3(0.0265, C5/C4 [PM3]).

7.3. 5-(4-Methylphenylazo)-3-Cyano-1-(H or Ethyl)-6-Hydroxy-4-Methyl-2-Pyridone

The AM1 method (Table 5(a)) of N-H derivatives indicates the following reactivity of tautomers in the reaction [**ene**] (S^E, bond):

HYD1(0.0291, C2=C6) > HYD2(0.0286, C2=C6) ≈ HYD3(0.0285, C2=C6) > AZO2(0.0277, C2=C6)

In the PM3 method, the order is as follows (S^E, bond, Table 5(b)):

HYD1(0.0284, C5=C6) ≈ HYD2(0.0283, C5=C4) > HYD3(0.0279, C5=C4) > AZO2(0.0200, C1=C3)

and indicates a different reaction site with the electrophilic agent $^1O_2$. The PM3 method indicates the reaction proceeds on the C5=C6 bond adjacent to the N(H)7-N8 hydrazone bond. In the AM1 method, the reaction should take place in the phenyl ring. NEt derivatives should react differently (Table 6(a) and Table 6(b)). The presence of an ethyl substituent in the 2-pyridone ring makes it the place most susceptible to $^1O_2$ oxidation. Both in the AM1 (Table 6(a)) and PM3 (Table 6(b)) methods, the C15/C16 substituent (Et) in the AZO2 tautomer should be oxidised first, then in AZO1 and HYD3. Then, the reaction would take place in the AZO2 and AZO1 tautomer at the C3=C4 (AM1) or C2=C6 (PM3) position.

[**AM1**, Table 6(a)]

AZO2(0.0310, Et) > AZO1(0.0304, Et) > HYD3(0.0291, Et) > HYD3(0.0287, C2=C6) > AZO2(0.0280, C3=C4) > AZO1(0.0274, C3=C4)

[**PM3**, Table 6(b)]

HYD3(0.0281, C5=C6) > AZO2(0.0274, Et) > AZO1(0.0270, Et) > HYD3(0.0253, Et) > AZO2(0.0209, C2=C6) > AZO1(0.0207, C3=C4)

In the calculations of the electronic structure of dyes and their reactivity, the AM1 and PM3 methods were used to predict their electronic properties, geometric structure, total energy and enthalpy of formation. The calculations did not consider the dyes interaction with fibers or with the products of their photochemical decomposition. The calculations were conducted assuming that the molecules are in a vacuum. They made it possible to obtain the HOMO and LUMO frontier electron density orbitals and calculate their superdelocalisibility coefficients based on the known values of the electron densities f^E and f^N, as well as the HOMO and LUMO energies. The higher these values are, the greater the probability of a reaction on a carbon or nitrogen atom using one of the active oxygen species.

By uv-vis spectrophotometric methods, it is possible to observe changes in absorption and their intensity (molar extinction < ε_{max}) within the ranges assigned to individual AZO, HYD tautomers, which are, however, resulting from the overlapping of many partial bands, assigned to all AZO or HYD tautomers. This is due to the fact that the aformentioned bands (AZO, HYD) maintain almost the same values of their absorption maximum λ_{max} [80] [81].

AZO1, AZO2 dyes are lactam tautomers of the AZO3 lactim form, HYD1, HYD2 dyes are lactim tautomers, HYD3 is a lactam tautomer. According to literature data [42], the lactim form with aromatic structure should be the most (e.g. AZO3).

The performed calculations show that the attack of the oxidising agent can take place on the carbon atom in the pyridone or phenyl ring. The reaction is accompanied by significant changes in the electronic structures of the molecules. We performed calculations of molecular reactivity to photooxidation of probable

forms of tautomeric azo dyes, derivatives of NH- and NEt-pyridones-2. These dyes can exist in equilibrium of azo-hydrazone and lactam-lactim tautomeric forms, and their proportions depend on several factors such as the nature of diazo compounds and their substituents, the temperature, or the solvent. They can exist in the form of six tautomers, for NH-pyridone-2 derivatives, and three for NEt-pyridone-2. As the calculations showed, the dyes in question occur mainly in the form of AZO1 and HYD3, while the other tautomers play a less significant role.

Literature data indicate that under certain conditions, this equilibrium may be completely shifted towards one of these tautomers. However, our calculations indicate that a state in which one of the forms predominates and the dye is present in a mixture is more likely. This is evidenced by the small energy difference between the tautomers,

The analysis of the performed calculations concerning the processes of electrophilic ($^1O_2$) and nucleophilic ($O_2^{\bullet -}$) photooxidation of selected azo derivatives of 2-pyridone leads to different conclusions.

Each method, AM1 or PM3, suggests a different reaction course, especially in the presence of a strongly accepting substituent in the phenyl residue, which is the -NO_2 group (σ_p = 0.78). In this case, the PM3 method suggests that the decomposition should occur first in the aromatic ring, only the ethyl substituent (Et) in the Net-2-pyridone residue would undergo the reaction next. In other cases (σ_p = H, CH_3), the ethyl group would undergo the oxidation reaction first, then the next process may take place in the phenyl ring of the phenylazo residue.

The tested dyes, as is also evident from other publications and experimental studies, should be present mainly in the HYD hydrazone form. In the AM1 method, such forms have the lowest enthalpies of formation, while in PM3 such forms should be AZO forms. It is characteristic, however, that in both methods, the form of HYD1 and AZO1 differ slightly in energy, which may suggest that their equilibrium is unstable, and they can easily change one to the another.

None of these calculation methods suggest, however, that the oxidation reaction proceeds according to an oxidation mechanism of unsaturated bonds (the exception is the [**ene**] reaction of the NO_2 derivative in the PM3 method). Their reactivity is lower than that of the atoms in the phenyl or heterocyclic ring. The results of the calculations allow us to draw a conclusion on the influence of the substituents on the lightfastness of the dyes. The lowest lightfastness should be found in nitro derivatives, which have the highest reactivity in the electrophilic oxidation with singlet oxygen $^1O_2$ has the C1 atom, to which the E_A substituent is attached. The spatial structure of the dyes may also be important, a factor that is usually overlooked when interpreting the calculation results.

In the reaction of singlet oxygen $^1O^2$ with an amino group, the reaction can lead to nitroso or nitro derivatives, or possibly to epoxidation or 1,2-addition derivatives to the C=C bond. Consequently, it would be impossible to determine the reactivity or rate of decomposition of a given chemical compound, since the influence of substituents in the ring on the reaction course will vary from one site

to another. In addition, the possibility of 1,2-addition to the C=C bond should be taken into account if the values of Σf^N or ΣS^E of adjacent carbon atoms are higher than the value of the superdelocalisability coefficient of a single carbon atom, which would cause them to react according to the epoxidation mechanism. In such situations, the reaction can result in the cleavage of the double bond and the formation of aldehydes or ketones, and—with full mineralisation—carbon dioxide. High values of superdelocalisability on adjacent carbon atoms are observed in some dyes, suggesting the possibility of 1,2-addition.

The probalility of the reaction is indicated by a high value of the S^E (or S^N) coefficient on the relevant atom. The calculations show that the attack of the oxidising agent can also occur on nitrogen atoms. This is accompanied by significant changes in molecules electronic structure.

Lightfastness can be tested for the probability of attack by an electrophilic or nucleophilic oxidising agent. The analysis of changes in ΔE, HOMO/LUMO frontier electron density and respective superdelocalisability can satisfactorily explain the lightfastness of these dyes.

8. Conclusions

Using the AM1 and PM3 methods, we calculated the reactivity of these derivatives in the S^E electrophilic photooxidation with singlet oxygen $^1O_2$ and in the S_N nucleophilic reaction of with the anion radical $O_2^{\bullet -}$. The performed calculations indicate that the atom most sensitive to $^1O_2$ oxidation in the electrophilic reaction is the C9 carbon of the heterocyclic ring, followed by the C11 carbon atom with the -CN substituent, where a low electron density is observed (except for the *p*-NO_2 derivative). In the reaction result, the heterocyclic ring of the tautomers AZO1 ÷ AZO3, HYD1 ÷ HYD3 is disintegrated in NH- and NEt-pyridone-2 derivatives, when -CH_3, H substituents are present in the *para*- position of the diazo compound. In *p*-NO_2 derivative C1 carbon atoms in the aromatic ring are the most reactive, then the reaction should lead to the decomposition of the heterocyclic ring initiated by the reaction of singlet oxygen $^1O_2$ on the C9 carbon atom. However, in no case can one expect the disintegration of double bonds, *i.e.* [**ene**] type reactions, due to low S^E reactivity indices in the vicinity of C1, C9 and C11 atoms.

Photooxidation reaction according to the nucleophilic mechanism of S^N by means of the anion-radical $O_2^{\bullet -}$ should take place on the carbon atoms of the C=O group (AZO1, AZO2) or C-OH (AZO3) groups, leading to the decomposition of the heterocyclic ring (NH-pyridones) or on the atom -N7(H)- bond in the hydrazone form of dyes (HYD1 ÷ HYD3).

Next, the reaction should take place on the C12/C14 carbons (C=O) of the heterocyclic ring. As a result, the decomposition of the azo bond in the hydrazone form should be expected first, followed by the decomposition of the heterocyclic ring. In the S^N reaction, the course and direction of the reaction are not influenced by the type of substituent in the diazo compound, photooxidation reactions for all

derivatives (CH_3, H, NO_2) should occur in a similar way and according to a similar mechanism.

It should be expected that the reactivity of the tested dyes is very similar to the reactivity of azo dyes, where the nitrogen atom of the azo bond undergoes electrophilic reaction by singlet oxygen $^1O_2$, which was confirmed by of AM1 and PM3 calculations [36] [67].

The AM1 method allowed the calculation of ΔE (= E_{HOMO}[dye] − E_{LUMO}[$^1O_2$]) of the dyes studied, which is 2.611 - 3.786 eV, and 2.787 - 4.496 eV for PM3 and is below the dye reactivity limit ~6 eV.

Predicting the properties of dyes and their correlations with the calculated values by quantum-chemical methods has some limitations. For example, calculations are made for molecules in a vacuum, to omit the formation of intermolecular hydrogen bonds (IHB), neglecting the influence of the solvent, environment (e.g. dyed fabric), temperature, etc.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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