Dyes and Pigments 188 (2021) 109149

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: http://www.elsevier.com/locate/dyepig

^{15}N, ^{13}C and ^{1}H NMR study of tautomerism in 2-(phenyldiazenyl-4-substituted naphthalen-1-ols. Influence of substitution in passive components on azo-hydrazo tautomerism

Zdeňka Neuerová, Antonín Lyčka [*]

University of Hradec Králové, Faculty of Science, Rokitanského 62, CZ-500 03, Hradec Králové 3, Czech Republic

ARTICLE INFO

Dedicated to Prof. Dr. Antonín Klásek on the occasion of his 80th birthday.

Keywords:
Azo compounds
^{15}N
^{13}C and ^{1}H NMR
Azo-hydrazo tautomerism

ABSTRACT

The one- and two-dimensional ^{15}N, ^{13}C and ^{1}H NMR spectra of benzenediazonium chloride coupling product with 4-R-naphthalene-1-ols (R = NO_2 **(1)**, Br **(2)**, Cl **(3)**, H **(4)**, OCH_3 **(5)**) were measured and analysed. It was found that the reaction products exist predominantly in hydrazone forms. Contrary to previously published influence of substituents in diazonium salts, where more electron acceptor types of substituents cause increase contents of hydrazo forms, the situation in compounds **1**–**5** is completely opposite. Moreover, hydrazone content in 4-nitro-2-[(*E*)-(4-nitro-phenyl)diazenyl]naphtalen-1-ol (**6**) combining substitution both in position 4 of passive component and position 4 of active component (i. e. diazonium salt) is higher compared with that in 4-nitro-2-[(*E*)-(phenyl)diazenyl]naphtalen-1-ol (**1**).

1. Introduction

Since discovery of azo-hydrazo tautomerism by Zincke and Bindewald in 1884 [1], many attempts to quantify the content of both forms have been performed [2–39 and reference cited therein] using mainly VIS [2–4,5,6,7,8,9,10,11,12], IR [2–4,9] and NMR spectroscopies [13–16,17–20,21,22,23,9,24,12,25–27,28,29], x-ray data [20,30,31,12,28] and later also theoretical calculations 9,30–39. In nearly all cases, the influence of substituents on azo/hydrazo tautomeric equilibria has been studied for compound being substituted in so called ***active*** components (i.e. in diazonium salts) since a wide variety of substituted anilines is very easily available. The common conclusion is that electron accepting substituents in substituted benzenediazonium salts, typically nitro group, increase hydrazone form content in resulting azo dyes compared with benzenediazonium salts substituted by electron donating substituents [6,32,10,29], e. g. methoxy or amino groups.

The aim of this paper is to characterize azo/hydrazone forms content in compounds having substituents in so called ***passive*** component, in 4-substituted naphthalene-1-ols, using very detailed one- and two-dimensional ^{15}N, ^{13}C and ^{1}H NMR spectra applications (Scheme 1).

2. Experimental

2.1. Synthesis

Starting 4-substituted-naphthtalene-1-ols were commercial products bought from Sigma-Aldrich company.

4-Nitro-2-[(*E*)-phenyldiazenyl]naphtalene-1-ol (**1**) [24], 4-bromo-2-[(*E*)- phenyldiazenyl]naphtalen-1-ol (**2**) [40], 4-chloro-2-[(*E*)-phenyldiazenyl]naphtalen-1-ol (**3**) [40], and 4-methoxy-2-[(*E*)-phenyldiazenyl]naphtalen-1-ol (**5**) [41] were prepared by coupling benzendiazonium chloride in water medium and 4-nitro-2-[(-*E*)-(4-nitro-phenyl)diazenyl]naphtalen-1-ol (**6**) [42] was prepared by coupling 4-nitrobenzendiazonium chloride, also in water medium. During coupling benzenediazonium chloride with naphthtalen-1-ol in water [43], 4-[(*E*)-phenyldiazenyl]naphthalen-1-ol is the main reaction product and 2-[(*E*)-phenyldiazenyl]naphtalen-1-ol (**4**) is only a by-product its content being usually less than 2%. K. Bredereck [44] proposed to perform the coupling reaction in a dichloromethane/water mixture, 2-[(*E*)- phenyldiazenyl]naphtalen-1-ol (**4**) being extracted into dichloromethane and giving 24% yield after column chromatography.

Melting points as well as yields of prepared compounds were in accordance with literature data and uniformity of compounds was checked by ^{1}H NMR spectroscopy.

---

[*] Corresponding author.
E-mail address: antonin.lycka@uhk.cz (A. Lyčka).

https://doi.org/10.1016/j.dyepig.2021.109149
Received 21 December 2020; Received in revised form 10 January 2021; Accepted 11 January 2021

2.2. NMR spectroscopy

The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer operating at 400.13 MHz for ^{1}H, 100.62 MHz for ^{13}C and at 40.56 MHz for ^{15}N and using liquid nitrogen-cooled 5-mm Prodigy cryo probe (Bruker) at 300 K. The samples were dissolved in deuteriochloroform. The ^{1}H and ^{13}C chemical shifts were referenced to internal TMS ($\delta = 0.00$). The ^{15}N chemical shifts were referred to the signal of external nitromethane placed in a co-axial capillary ($\delta = 0.0$). All 2D experiments (gradient-selected (gs)-COSY, gs-NOESY, gs-HMQC, gs-HSQC, gs-HSQC-TOCSY, gs-HMBC) and 1D ^{1}H–^{15}N gs-HSQC were performed using manufacturer's software (TOPSPIN 3.5) [45–47].

3. Results and discussions

Azo-hydrazo tautomerism is a typical feature of azo dyes containing hydroxy group in an appropriate position(s). In most cases, the influence of substituents on azo/hydrazo tautomeric equilibria has been studied for compound being substituted in so called active components (i.e. in diazonium salts) since a wide variety of substituted anilines is very easily available.

In this paper, we study one- and two-dimensional ^{15}N, ^{13}C and ^{1}H NMR spectra in compounds **1**–**5** (Scheme 1) prepared by coupling of benzenediazonium chloride with 4-substituted naphthalen-1-ol. The substituents were chosen in such a manner so that we could cover non-substituted naphthalen-1-ol, one strongly electron accepting substituent (NO_2), two halogenes and one very electron donating substituent (OCH_3).

The one- and two-dimensional ^{15}N, ^{13}C and ^{1}H NMR spectra of compounds **1**–**5** were measured and very thoroughly analysed. 2D gradient-selected (gs)-COSY, gs-NOESY, gs-HMQC, gs-HSQC, gs-HSQC-TOCSY and gs-HMBC) and 1D ^{1}H–^{15}N gs-HSQC were performed. The obtained results are collected in Table 1.

Lin et al. [24] performed ^{1}H and ^{13}C NMR study of a set of ten 1-[(*E*)-(3- or 4-subst. phenyl)diazenyl]naphtalen-2-ol in several solvents. Azo/hydrazone forms content estimation is based on changes of ^{13}C chemical shifts of carbon C(2) = O/C(2)-OH. We cannot use this approach since ^{13}C chemical shifts of carbon C(1) = O/C(1)-OH in compounds **1**–**5** are strongly influenced by substituent chemical shifts (SCS) effect of substituents R from position 4 (SCS for nitro group is +6.8 ppm, for bromine −0.2 ppm, while SCS for methoxy group is – 7.6 ppm) [48]. After "a correction" of experimental ^{13}C chemical shifts for C-1, we can obtain the following monotonously increasing values of C(1) = O/C(1)-OH 165.0, 173.2, 174.2 and 184.6 ppm for compounds **1, 2** and **4, 5**. On the other hand, we could use ^{13}C chemical shifts of carbon C(2′) or C(4′) of phenyl group present in all compounds **1**–**5**, however, the differences are rather small (Table 1).

Much greater changes in $^1J(^{15}N_\alpha, {}^1H)_{exp}$ coupling constants and ^{15}N chemical shifts of N_α and N_b for compounds **1**–**5** are collected in Table 2. Hydrazone form content was calculated using equation (1) using $^1J(^{15}N_\alpha, {}^1H)_H = 96.5$ Hz as proposed by Bekárek et al. [15,16] measured for 5-methyl-2-phenyl-4-(2-phenylhydrazono)-2,4-dihydro-3H-pyrazol-3-one in deuteriochloroform.

$$\%Hydrazone = \left[\,{}^1J\left(15N_\alpha,\ {}^1H\right)\mathrm{exp} \,/\, {}^1J\left(\left(15N_\alpha,\ {}^1H\right)_H\right)\right]{*}100 \tag{1}$$

The results are shown in Table 2 differing from 63.5% for **1**–91.2% for **5**.

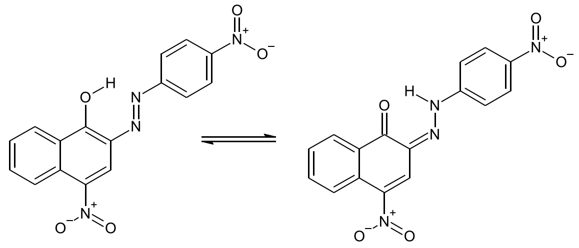
Analogously, ^{15}N chemical shifts of N_α and N_β were used for hydrazone form content calculation [13,14,18] using Equation (2)

$$\%Hydrazone = \left[\delta\left({}^{15}N_{\alpha/\beta}\right)\mathrm{exp} - \left({}^{15}N_{\alpha/\beta}\right)H\right] / \left[\ \delta\left({}^{15}N_{\alpha/\beta}\right)A - \delta\left({}^{15}N_{\alpha/\beta}\right)H\right]{*}100 \tag{2}$$

The ^{15}N chemical shifts of N_α and N_β are again shown in Table 2 to demonstrate their changes and to calculate hydrazone forms contents. Weighted average values of hydrazone form content was calculated using all three results being subsequently used for determination of equilibrium constants K = [hydrazo form]/[azo form].

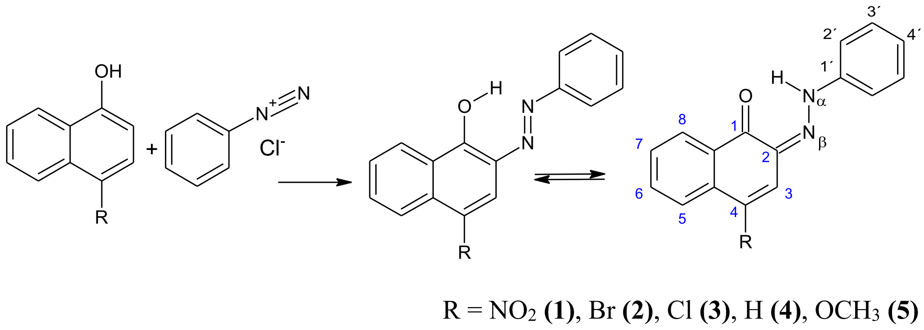
The calculated (average) hydrazo form contents differ considerable for compounds **1**–**5** being strongly substituent dependent. Previously published influence of substituents in diazonium salts showed that more electron acceptor types of substituents cause increase of hydrazo forms [6,32,10,29]. Lin et al. presented [24] an approximate correlation of K = [hydrazo form]/[azo form] on σ^+ Hammett constants. A part of it is presented in Fig. 1 having positive slope contrary to our data having negative slope of a curve. The correlation is not too precise, however, the opposite trends are clearly visible.

Hydrazone form content in compound **1,** having nitro group in position 4 of naphthalene, was ca 64% (Table 2). According to literature data mentioned above [6,32,10,29], an electron accepting group in position 4 of diazonium salt should increase hydrazone form content. To test this expectation also in our series of compounds, we prepared compound **6:**



The solubility of compound **6** in deuteriochloroform is very low, however, we succeeded in measuring $^1J(^{15}N, {}^1H)_{exp}$ and $\delta(^{15}N_\alpha)$ by long term accumulation of NMR spectra.

The value of $^1J(^{15}N, {}^1H)_{exp}$ coupling constant in compound **6** increased to 82.4 Hz compared with 63.5 Hz in compound **1** (Table 2) clearly proving the above-mentioned expectation that hydrazone form content should increase considerably. The calculated hydrazone form content is 85.4%. The experimental ^{15}N chemical shift of $\delta(^{15}N_\alpha)$ is −154.6 ppm (contrary to −108.9 ppm in compound **1**), and calculated



Scheme 1. R = NO_2 **(1)**, Br **(2)**, Cl **(3)**, H **(4)**, OCH_3 **(5)**.

Table 1
^{1}H,^{13}C and^{15}N chemical shifts (ppm) and $^{1}J(^{15}N, ^{1}H)_{exp}$ coupling constants (Hz, ± 0.3 Hz)) in compounds **1**–**5** in deuteriochloroform.

H/C	1 (NO_2)		2 (Br)		3 (Cl)		4 (H)		5 (OCH_3)	
	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$
1	16.71	171.8	16.08	173.4	16.08	173.8	16.10	174.2	15.72	177.0
2	–	129.3	–	132.7	–	132.0	–	132.8	–	132.7
3	8.46	130.0	7.61	131.1	7.33	127.0	7.19	128.3	6.39	101.5
4	–	139.2	–	114.1	–	123.9	6.98	121.0	–	149.3
4a	–	128.4	–	135.0	–	134.1	–	137.1	–	130.7
5	8.58	124.5	8.00	123.1	7.98	124.9	7.53	127.5	8.40	122.4
6	7.80	133.4	7.73	133.0	7.70	132.8	7.57	132.2	7.52	132.8
7	7.61	127.5	7.55	127.2	7.51	127.1	7.70	126.2	7.69	127.3
8	8.53	127.0	8.43	126.9	8.41	126.9	8.40	126.7	8.00	127.0
8a	–	129.6	–	130.8	–	130.7	–	130.2	–	132.6
$N_{\alpha}H$	16.71	−108.9[a]	16.08	−153.2[a]	16.03	−157.4[a]	16.10	−148.1[a]	15.72	−191.8[a]
$^{1}J(^{15}N_{\alpha},^{1}H)_{exp}$		63.5 [b]		79.4[b]		80.8[b]		77.3[b]		91.2[b]
N_{β}	–	40.1[c]	–	11.8[c]	–	8.7[c]	–	16.3[c]	–	−17.2[c]
1’	–	143.1	–	143.0	–	142.6	–	143.2	–	142.6
2’	7.74	119.2	7.62	117.8	7.57	117.5	7.60	117.6	7.52	116.1
3’	7.53	129.9	7.46	129.7	7.43	129.6	7.42	129.5	7.41	129.5
4’	7.42	129.5	7.29	127.2	7.26	126.9	7.23	126.7	7.16	124.9
R	–	−10.2[d]	–	–	–	–		–	3.97	55.4

[a] $\delta(^{15}N_{\alpha})$.
[b] $^{1}J(^{15}N_{\alpha}, ^{1}H)_{exp}$.
[c] $\delta(^{15}N_{\beta})$.
[d] $\delta(^{15}N)(NO_2)$.

Table 2
^{15}N Chemical shifts (ppm) and $^{1}J(^{15}N_{\alpha}, ^{1}H)_{exp}$ coupling constants (Hz, ± 0.3 Hz)) in compounds **1**–**5** and calculated hydrazone content in deuteriochloroform.

	1 (NO_2)	2 (Br)	3 (Cl)	4 (H)	5 (OCH_3)
$^{1}J(^{15}N_{\alpha}, ^{1}H)_{exp}$	63.5[a]	79.4[a]	80.8[a]	77.3[a]	91.2[a]
% H[a]	66.2	82.7	84.2	80.5	95.0
$\delta(^{15}N_{\alpha})$	−108.9	−153.2	−157.4	−148.1	−191.8
% H[b]	64.9	81.1	82.6	79.2	95.1
$\delta(^{15}N_{\beta})$	40.1	11.8	8.7	16.3	−17.2
% H[c]	60.2	79.9	82.0	76.7	100.0
Average $\bar{H}$[d]	**63.8**	**81.2**	**82.9**	**78.8**	**96.7**
K[e]	**1.8**	**4.3**	**4.9**	**3.7**	**29.3**

[a] Calculated hydrazo form content in % using $^{1}J(^{15}N_{\alpha}, ^{1}H)_{exp}$.
[b] Calculated hydrazo form content in % using $\delta(^{15}N_{\alpha})$.
[c] Calculated hydrazo form content in % using $\delta(^{15}N_{\beta})$.
[d] Average hydrazo form content calculated from values [a-c].
[e] K = [hydrazo form]/[azo form], ratio content calculated from average hydrazo form in % and [azo form] = 100 - [hydrazo form].

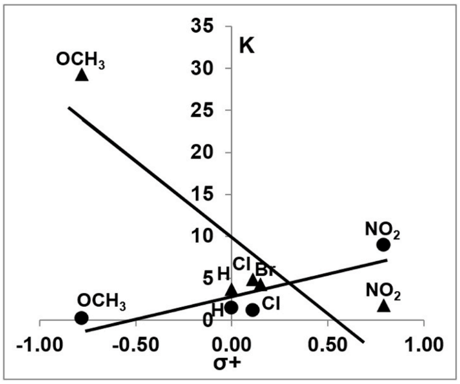


Fig. 1. Opposite dependence of K = [hydrazo form]/[azo form] on σ^{+} Hammett constants in 1-[(*E*)-(substituted phenyl)diazenyl]naphtalene-2-ols (presented by black circles [9]) and in 4-substituted-2-[(*E*)-phenyldiazenyl] naphtalene-1-ols **1**–**5** ((presented by triangles (this paper)).

hydrazone form content in compound **6** using this value is 81.6%. Both experimental and calculated data are agreement with a common expectation.

4. Conclusion

Very detailed analysis of data obtained from one- and two-dimensional ^{15}N, ^{13}C and ^{1}H NMR spectra allowed to characterize undoubtedly benzenediazonium chloride coupling products with 4-R-naphthalene-1-ols (R = NO_2 **(1)**, Br **(2)**, Cl **(3)**, H **(4)**, OCH_3 **(5)**). The $^{1}J(^{15}N, ^{1}H)_{exp}$ coupling constants and both $\delta(^{15}N_{\alpha})$ and $\delta(^{15}N_{\beta})$ values allowed us to prove that the reaction products exist predominantly in hydrazone forms and correspond to (2*Z*)-4-R-2-[2-(phenyl)hydrazinylidene]naphthalen-1(2*H*)-ones **1**–**5**. Contrary to previously published influence of substituents in diazonium salts, more electron acceptor type of substituents cause an increase of azo forms. Hydrazone content in dinitro derivative (2*Z*)-4-nitro-2-[2-(4-nitrophenyl)hydrazinylidene] naphthalen-1(2*H*)-one **6** is higher compared with that in mono nitro (2*Z*)-4-nitro-2-[2-(phenyl)hydrazinylidene]naphthalen-1(2*H*)-one **1** indicating the fact that substitution of active component by nitro group in position 4 increases hydrazone form content also in our model system.

Declaration of competing interest

The authors declare no conflict of interests.

Acknowledgement

The authors thank the Faculty of Science, University of Hradec Králové for a support.

References

[1] Zincke T, Chem Bindewald H. Ber 1884;17:3026.
[2] Antonov L. Tautomerism: methods and theories. first ed. Weinheim: Wiley-VCH; 2013, ISBN 978-3-527-33294-6. p. 400.
[3] Ball P, Nicholls CH. Azo-hydrazone tautomerism of hydroxyazo compounds—a review. Dyes Pigments 1982;3:5–26. https://doi.org/10.1016/0143-7208(82)80010-7.
[4] Zollinger H. Color chemistry: syntheses, properties, and applications of organic dyes and pigments. 3rd rev., vol. 637. Weinheim: Wiley-VCH; 2003, ISBN 3906390233.

[5] Reeves RL, Kaiser RS. Selective solvation of hydrophobic ions in structured solvents. Azo-hydrazone tautomerism of azo dyes in aqueous organic solvents. J Org Chem 1970;35:3670–5. https://doi.org/10.1021/jo00836a017.

[6] Haessner R, Mustroph H, Borsdorf R. Study on the UV-VIS spectral behavior of azo dyes 8. Quantitative study on tautomerically substituted 1-phenylazo-2-naphthol by means of UV-VIS spectroscopy. Dyes Pigments 1985;6:271–91. https://doi.org/10.1016/0143-7208(85)87004-2.

[7] Antonov resolution of overlapping UV-visible absorption bands: quantitative analysis of tautomeric equilibria L. Stoyanov S. Anal. Chim. Acta 1995;314:225–32. https://doi.org/10.1016/0003-2670(95)00281-4.

[8] Nedelcheva D, Antonov L, Lyčka A, Damyanova B, Popov S. Chemometric models for quantitative analysis of tautomeric Schiff bases and azo dyes. Curr Org Chem 2009;13:217–39. https://doi.org/10.2174/138527209787314832.

[9] Almeida MR, Stephani R, Dos Santos HF. de Oliveira LFC Spectroscopic and theoretical study of the "azo"-dye E124 in condensate phase: evidence of a dominant hydrazo form. J Phys Chem A 2010;114:526–34. https://doi.org/10.1021/jp907473d.

[10] You W, Zhu H-Y, Huang W, Hu B, Fan Y, You X-Z. The first obserwation of azo-hydrazone and cis-trans tautomerisms for disperse yellow dyes and their nickel(II) and copper(II) complexes. Dalton Trans 2010;39:7876–80. https://doi.org/10.1039/c0dt00101e.

[11] Aysha T, Luňák Jr S, Lyčka A, R Synthesis Hrdina. Absorption and fluorescence of hydrazone colorants based on pyrrolinone esters. Dyes Pigments 2011;91:170–6. https://doi.org/10.1016/j.dyepig.2011.03.013.

[12] Wu Z, Zhang R, Rong Z. Azo-hydrazone tautomerism of azo dyes huagong xuebao/CIESC journal. 2015-01-01. https://doi.org/10.11949/j.issn.0438-1157.20140958.

[13] Lyčka A. Multinuclear NMR of azo dyestuffs. Annu Rep NMR Spectrosc 1993;26:247–81. 978-0-12-505326-6.

[14] Lyčka A. Multinuclear NMR of azo dyes and their metal complexes. Annu Rep NMR Spectrosc 2000;42:1–57. 978-0-12-505342-6.

[15] Bekárek V, Rothschein K, Vetešník P. Večeřa M Estimation of azo - hydrazo tautomeric equilibrium in ortho-hydroxy-azo compounds by N.M.R. Tetrahedron Lett 1968;9:3711–3. https://doi.org/10.1016/S0040-4039(00)75523-7.

[16] Bekárek V, Dobáš J, Socha J, Vetešník P. Večeřa M Reactivity of organic azo-compounds.10. NMR study on azo-hydrazone tautomeric equilibrium in hydroxy azo-compounds. Collect Czech Chem Commun 1970;35:1406. https://doi.org/10.1135/cccc19701406.

[17] Lyčka A, Šnobl D, Macháček V. Večeřa M ^{15}N NMR study of azo-hydrazone t automerism of ^{15}N -labelled azo dyestuffs. Org Magn Reson 1981;15:390–3. https://doi.org/10.1002/mrc.1270150413.

[18] Lyčka A, Šnobl D, Macháček V. Večeřa M ^{15}N NMR study of azo-hydrazone tautomerism of ^{15}N -labelled azo dyestuffs. Org Magn Reson 1981;16:17–9. https://doi10.1002/mrc.1270160106.

[19] Kelemen J, Moss S, Sauter H, Winkler T. Azo-hydrazone tautomerism in azo dyes. II. Raman, NMR and mass spectrometric investigations of 1-phenylazo-2-naphthylamine and 1-phenylazo-2-naphthol derivatives. Dyes Pigments 1982;3:27–47. https://doi.org/10.1016/0143-7208(82)80011-9.

[20] Kelemen J, Kormany G, Rihs G. Azo-hydrazone tautomerism in azo dyes. III. The tautomeric structure of adsorbed 1-(4'-nitrophenylazo)-2-naphthylamine from crystal structure determination. Dyes Pigments 1982;3:249–71. https://doi.org/10.1016/0143-7208(82)80001-6.

[21] Šimůnek P, Bertolasi V, Lyčka A, Macháček V. An NMR and X-ray study of structure of azo coupling product from 4-dimethyl-aminopent-3-en-2-one and benzenediazonium tetrafluoroborate. Org Biomol Chem 2003:3250–6. https://doi.org/10.1039/B303206J.

[22] Šimůnek P, Svobodová M, Bertolasi V, Pretto L, Lyčka A, Macháček V. Structure and tautomerism of azo coupuling products from N-alkylenaminones derived from acetylacetone and benzoylacetone in solid phase and solution. New J Chem 2007;31:429–38. https://doi.org/10.1039/B613346K.

[23] Loghmani-Khouzania H, Mehrabia H, Sadeghia MMM. Gawinecki R study of hydrazone-hydrazoimine tautomerism in α-Azo-6-ketomethylphenanthridines. J Iran Chem Soc 2009;6:129–37. https://doi.org/10.1007/BF03246511.

[24] Lin Y-C, Chen C-C, Ding M-F, Lin S-T. The substituent effect of 1-Arylazonaphthen-2-ols on azo-hydrazone tautomerization according to NMR analysis. J Chin Chem Soc 2015;62:335–41. https://doi.org/10.1002/jccs.2014003.

[25] Lyčka A. 4-Carboxyl-2,6-dinitrophenylazohydroxynaphathalenes tautomerism NMR re-explained. Dyes Pigments 2017;142:51–4. https://doi.org/10.1016/j.dyepig.2017.03.003.

[26] Lyčka A ^{15}N NMR study of (E)- and (Z)-2-(2-(2-hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,3-diones. A suitable method for analysis of hydrazone isomers. Dyes Pigments 2018;150:181–4. https://doi.org/10.1016/j.dyepig.2017.10.023.

[27] Deneva V, Lyčka A, Hristova S, Crochet A, Fromm KM. Antonov L Tautomerism in azo dyes: border cases of azo and hydrazo tautomers as possible NMR reference compounds. Dyes Pigments 2019;165:157–63. https://doi.org/10.1016/j.dyepig.2019.02.015.

[28] Debnath P, Singh KS, Devi TS, Singh SS, Butcher RJ, Sierond L, Maniukiewiczd W. Synthesis, characterization, crystal structures and anti-diabetic activity of organotin (IV) complexes with 2-(4-hydroxynaphthylazo)-benzoic acid. Inorg Chim Acta 2020;510:119736. https://doi.org/10.1016/j.ica.2020.119736.

[29] Marek R. Lyčka A ^{15}N NMR spectroscopy in structural analysis. Curr Org Chem 2002;6:35–66. https://doi.org/10.2174/1385272023374643.

[30] Antonov L, Kawauhi S, Satoh M, Komijama J. Theoretical investigations on the tautomerism of 1-phenylazo-4-naphthol and its isomers. Dyes Pigments 1999;40:163. https://doi.org/10.1016/S0143-7208(98)00044-8.

[31] Gili P, Bertolasi V, Pretto L, Lyčka A, Gilli G. The nature of solid-state N-H…O/O-H…N tautomeric competition in resonant systems. Intramolecular proton transfer in low-barrier hydrogen bonds formed by the …O=C-C=N-NH… ↔…HO-C=C-N=N… ketohydrazone-azoenol systém. A variable-temperature X-ray crystallographic and DFT computational study. Am. Chem. Soc. 2002;124:13554–67. https://doi.org/10.1021/ja020589x.

[32] Mazurek AP, Skulski L. Dobrowolski JCz Tautomeric azo-hydrazo equilibria in 8-arylazotheophyllines: theoretical and experimental studies. J Mol Struct 1997;410–411:421–4. https://doi.org/10.1016/S0022-2860(96)09500-2.

[33] Özen AS, Doruker P, Aviyente V. Effect of cooperative hydrogen bonding in azo−hydrazone tautomerism of azo dyes. J Phys Chem A 2007;111:13506–14. https://doi.org/10.1021/jp0755645.

[34] Ferreira GR, Garcia HC, Couri Mrc MRC, Dos Santos H, de Oliveira LFC. On the azo/hydrazo equilibrium in Sudan I azo dye derivatives. J Phys Chem A 2013;117:642–9. https://doi.org/10.1021/jp310229h.

[35] Lyčka A, Luňák S, Aysha T, Holuša R, Hrdina R. A ^{1}H, ^{13}C and ^{15}N NMR spectroscopic and GIAO DFT study of ethyl 5-oxo-2-phenyl-4-(2-phenylhydrazono)-4,5-dihydro-1*H*-pyrrole-3-carboxylate. Tetrahedron Lett 2010;51:3149–51. https://doi.org/10.1016/j.tetlet.2010.04.043.

[36] Mansouria L, Zouchounea B. Substitution effects and electronic properties of the azo dye (1-phenylazo-2-naphthol) species: a TD-DFT electronic spectra investigation. Can J Chem 2015;93:5. https://doi.org/10.1139/cjc-2014-0436.

[37] Wojciechowski K, Szuster L. Azo-hydrazo tautomerism and structure of selected metal complex dyes AM1 and ZINDO/1 Methods Computational Chemistry, vol. 4; 2016. p. 97–118. https://doi.org/10.4236/cc.2016.44010. http://www.scirp.org/journal/cc.

[38] Antonov L. 12. Tautomerism in azo and azomethyne dyes: when and if theory meets experiment Molecules, vol. 24; 2019 Jun. p. 2252. https://doi.org/10.3390/molecules24122252. Published online 2019 Jun 17.

[39] Hansen PE, Saeed BA, Rutu RS, Kupka T. One-bond $^{1}J(^{15}$N,H) coupling constants at sp^{2}-hybridized nitrogen of Schiff bases, enaminones and similar compounds: a theoretical study. Magn Reson Chem 2020;58:750–62. https://doi.org/10.1002/mrc.5052.

[40] Mitchell AD, Smith C. Constitution of hydroxyazo-compounds. Action of mercuric acetate on benzeneazonaphtols. J Chem Soc 1909:1430–7.

[41] Ebine S. 3,4-Benzotropolone and related compounds. IV. Azo- and hydroxy-3,4-benzotropolones. Bull Chem Soc Jpn 1965;38:2029–34. https://doi.org/10.1246/bcsj.38.2029.

[42] Inoue A, Kuroku N, Konishi K. Studies on the dyes derived from 1,4-naphtoquinone. Bull. Univ. Osaka Prefect., Ser. A 1959;8:31–54.

[43] Schündehütte KH. Diarylazoverbindungen. In: Stroh R. Methoden der Organischen chemie (Houben-Weyl), vol. 3. Stuttgart: Georg Thieme Verlag; 1956. p. 213–466.

[44] Bredereck, K.; Selim, K Process for preparation of azo dyes. IPC: C09B43/11. GB2058814.

[45] Berger S, Braun S. 200 and more basic NMR experiments: a practical course. third ed. Weinheim: Wiley-VCH; 2004, ISBN 978-3-527-31067-8.

[46] Claridge TDW. High-resolution NMR techniques in organic chemistry. third ed. Elsevier; 2016, ISBN 9780080999869.

[47] Jacobsen NE. NMR data interpretation explained. New Jersey: Wiley; 2016, ISBN 9781118370223.

[48] Seita J, Sandström J, Drakenberg T. Org Magn Reson 1978;11:239–45. https://doi.org/10.1002/mrc.1270110505.