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The synthesis and structural study of two benzothiazolyl azo dyes: X-ray crystallographic and computational study of azo–hydrazone tautomerism

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ABSTRACT

The synthesis, FT-IR, ^{1}H and ^{13}C NMR characterisation, as well as crystal and molecular structure determined by single-crystal X-ray diffraction data, of two azo dyes derived from 6-aminobenzothiazole: 6-[(4-*N*,*N*-dimethylaminophenyl)diazenyl]benzothiazole and 6-[(2-hydroxy-1-naphthyl)diazenyl]benzo thiazole are reported. Both dyes are essentially planar with the exclusion of methyl groups in 6-[(4-*N*,*N*-dimethylaminophenyl)diazenyl]benzothiazole, which exibits 100% *E*-configuration in terms of orientation of the substituents about the central azo linkage. Single-crystal X-ray study of 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole was undertaken to established whether the hydrazone or azo tautomer was present in the solid state as well as any potential shift in tautomeric equilibrium imparted by temperature variation (296 and 100 K). Density functional theory calculations revealed that the hydrazone tautomer was more stable than the azo tautomer and that the tautomeric equilibrium was shifted towards the hydrazone form at lower temperature.

1. Introduction

Aromatic and heteroaromatic azo compounds constitute the largest and the most diverse group of synthetic dyes with application not only as textile colorants but in many other industrial fields for coloring different substrates, biological-medical studies, in the field of non-linear optics and optical data storage [1–3]. The interest for benzothiazole azo dyes as disperse and cationic dyes for textile application is growing [4].

On the other hand, detailed knowledge of molecular structure is inevitable for finding the structure–function relationships and for a systematic approach to the design of new dyes [5–7]. Structural information obtained from single-crystal X-ray diffraction analysis including conformation, stereochemistry, intra- and inter- molecular interactions are in relation with optical properties as well as with technical properties of azo dyes and pigments [8,9]. The azo–hydrazone tautomerism in azo dyes has been known for more than a hundred years and is directly connected with the presence of at least one protic donor group in conjugation to the azo bridge (i.e. 2-naphthol) [10]. The azo–hydrazone tautomerism is quite interesting from a theoretical and practical point of view because the two tautomers have different properties. The present tautomer could be responsible for N–N or C–N bonds cleavage during the bleaching process. A. S. Özen and co-authors [11] established by DFT calculations that the bleaching process starts *via* attack to the azo N atom and causes the cleavage of the N–N bond rather than the C–N bond, in the case of the azo tautomeric form. The presence of the hydrazone tautomeric form will cause the C–N bond cleavage. Therefore, the tautomeric form of azo dyes play one of the crucial role in designing efficient oxidation processes that could minimize the toxicological effects such as formation of carcinogenic amines.

As a part of our continuous interest in the synthesis, crystallography, biological and optical evaluation of benzothiazole compounds we embarked on the present crystallographic study this research [12–15]. Here, we report the synthesis and crystal and molecular structure of two dyes derived from 6-aminobenzothiazole: 6-[(4-*N*,*N*-dimethylaminophenyl)diazenyl]benzothiazole (**1**) and 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole (**2**). With this investigation, together with computational study, we established that there is preference of one tautomer over another. The crystal structures of **1** and **2** on the basis of C–H···N, C–H···O and π···π interactions have been discussed.

2. Experimental

2.1. Synthesis

6-Aminobenzothiazole was prepared as described in the literature [16]. UV–Vis spectra were recorded on a Perkin–Elmer

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Lambda 2 spectrophotometer for solution in ethanol. The ^{1}H NMR and the ^{13}C NMR spectra were recorded with a Brucker Avance DPX-300 (300 MHz and 75.5 MHz, for ^{1}H and ^{13}C respectively) in DMSO-d_6. Chemical shifts are reported in ppm relative to TMS as an internal standard. IR spectra were recorded with Nicolet Magna 760 spectrophotometer as KBr pellets. Elemental analyses were performed at the microanalytical laboratories of the "Ruđer Bošković" Institute. Melting points were determined on a Kofler block apparatus.

2.1.1. 6-[(4-N,N-dimethylaminophenyl)diazenyl]benzothiazole (**1**)

A solution of 6-aminobenzothiazole (3 g, 0.02 mol) in water (15 mL) and conc. HCl (6 mL) was cooled to 0–5 °C and with stirring a solution of $NaNO_2$ (1.7 g, 0.024 mol) in water (10 mL) was added dropwise. The mixture was stirred for 30 min and used immediately for coupling reaction.

To the stirred diazonium solution cooled at 5 °C *N,N*-dimethylaniline (2.7 mL, 0.021 mol) was added dropwise over 15 min. The solution of NaOAc (5.0 g, 0.03 mol) in water (10 mL) was added over 2 h to the reaction mixture at 10–15 °C. The stirring was continued for 1 h at room temperature. The reaction mixture was made alkaline with 10% solution of NaOH, and the precipitate were filtered off, washed with water, and dried under vacuum. The crude product was purified by column chromatography on SiO_2 with CH_2Cl_2/acetone (10/0.5) to give pure product as orange solid. Yield 2.4 g (46.4%); m.p. 139–140 °C. UV/Vis (EtOH): λ_{max}/nm = 425, ε/L mol^{-1} cm^{-1} = 35 000. IR (KBr): υ/cm^{-1} = 3050, 2920, 2852, 1605. ^{1}H NMR (DMSO-d_6, 300 MHz): δ/ppm = 9.45 (s, 1H), 8.54 (d, 1H, J = 1.7 Hz), 8.16 (d, 1H, J = 8.7 Hz), 7.97 (dd, 1H, J = 1.8 Hz, J = 8.7 Hz), 7.81 (d, 2H, J = 9.0 Hz), 6.82 (d, 2H, J = 9.0 Hz), 3.04 (s, 6H). ^{13}C NMR (DMSO-d_6, 75.5 MHz): δ/ppm = 154.1 (s), 153.1 (s), 150.5 (s), 143.1 (s), 135.2 (s), 125.3 (d, 2C), 123.9 (d), 120.3 (d), 117.2 (d), 112.0 (d, 2C), 40.3 (q, 2C). Anal. Calcd for $C_{15}H_{14}N_4S$ (282.3): C, 63.80; H, 5.00; N, 19.84. Found: C, 63.94; H, 4.83, N, 19.86.

2.1.2. 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole (**2**)

To a stirred solution of 2-naphthol (3 g, 0.021 mol) in 10% NaOH (40 mL) was slowly added previously prepared diazonium salts solution of 6-aminobenzothiazole at 5 °C and stirring was continued for 30 min. The reaction mixture was pured in water (200 mL), and the precipitate was filtered off, washed with water, and dried. Crystallization twice from xylene (charcoal) afforded pure product as orange-red solid. Yield 3.85 g (63.1%); m.p. 193–195 °C. UV/Vis (EtOH): λ_{max}/nm = 480, ε/Lmol^{-1}cm^{-1} = 18 000. IR (KBr): υ/cm^{-1} = 3433, 3039, 1621. ^{1}H NMR (DMSO-d_6, 300 MHz): δ/ppm = 15.61 (s, 1H), 9.46 (s, 1H), 8.80 (d, 1H, J = 1.9 Hz), 8.70 (d, 1H, J = 8.1 Hz), 8.23 (d, 1H, J = 8.8 Hz), 8.11 (dd, 1H, J = 2.1 Hz, J = 8.8 Hz), 8.01 (d, 1H, J = 9.3 Hz), 7.84 (d, 1H, J = 7.8 Hz), 7.66 (dd, 1H, J = 8.2 Hz, J = 8.3 Hz), 7.50 (dd, 1H, J = 8.0 Hz, J = 8.1 Hz), 7.02 (d, 1H, J = 9.3 Hz). ^{13}C NMR (DMSO-d_6, 75.5 MHz): δ/ppm = 166.7(s), 158.3(d), 153.4(s), 144.2(s), 140.0(d), 135.8(s), 133.2(s), 129.9(s), 129.6(d), 129.4(d), 128.5(s), 126.3(d), 124.5(d), 123.7(d), 122.1(d), 118.8(d), 114.1(d). Anal. Calcd for $C_{17}H_{11}N_3OS$ (305.3): C, 66,87; H, 3.63; N, 13.76. Found: C, 66.85; H, 3.82, N, 13.71.

2.2. X-ray crystallography

Crystallographic data and selected bond lengths and angles are given in Tables 1 and 2 for compound **1** and in Tables 3 and 4 for compound **2**. Hydrogen bond geometry is listed in Table 5 for both compounds. Crystallographic data were recorded on a Xcalibur diffractometer, equipped with a CCD area detector, using Mo Kα radiation (λ = 0.71073 Å) at T = 296 K for **1** and by using Cu Kα radiation (λ = 1.54184 Å) at two temperatures T = 296 and 100 K in order to follow up tautomeric effects for compound **2**. Lorentz and polarization correction (CryAlis RED) [17] was applied. Structures were solved by direct methods (SHELXS97) [18] and refined by full-matrix least squares against F^2 using all data (SHELXL97) [18]. The central azo linkage exhibits positional disorder of the N2 and N3 nitrogen atoms in compound **1**. The two possible positions of each N2 and N3 atoms (N2a and N2b; N3a and N3a) have been resolved and refined by using SHELXL97 PART instruction. The occupational factor has been refined revealing 9:1 distribution of two possible positions of the azo linkage. The bond distances N2b–C5 and N3b–C8 have been restrained to 1.425 Å with the s.u. of 0.005. The atom positions N2b and N3b were refined isotropically, and all other non-H atoms were refined anisotropically.

All the hydrogens were fixed geometrically, with C_{Ar}–H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C), and made to ride on their parent atoms in both structures. The hydrogen atom that belongs to O1 or N2 atom in compound **2** was located in an electron-density Fourier map as

Table 1
General and crystal data and summary of intensity data collection and structure refinement for compound **1**.

Formula	$C_{15}H_{14}N_4S$
M_r	282.37
Crystal system, colour and habit	Monoclinic, red, irregular block
Space group	$P\,2_1/a$ (No. 14)
Crystal dimensions (mm)	0.34 × 0.27 × 0.24
Unit cell parameters:	
a (Å)	12.6706(11)
b (Å)	6.5601(7)
c (Å)	16.3926(14)
β/o	93.643(7)
V (Å^3)	1359.8(2)
Z	4
D_c (gcm^{-3})	1.379
μ (mm^{-1})	0.233
F(000)	592
2θ range for data collection (°)	4–27
h,k,l range	−16 to 16; −8 to 8; −20 to 20
Scan type	ω
No. measured reflections	15 411
No. independent reflections (R_{int})	2944, 0.035
No. refined parameters	192
No. observed reflections, $I \geq 2\sigma(I)$	2663
g_1, g_2 in w	0.0551, 0.8160
R, wR [$I \geq 2\sigma(I)$]	0.0645, 0.1499
R, wR [all data]	0.0716, 0.1449
Goodness of fit on F^2, S	1.15
Max., min. Electron-density (e Å^{-3})	−0.39, 0.27
Maximum Δ/σ	< 0.001

Table 2
Selected interatomic distances (Å) and valence and torsion angles (°) for the compound **1**.

Selected bond distances	
N2a–N3a	1.224(3)
S1–C1	1.734(3)
S1–C7	1.729(2)
N1–C1	1.286(3)
N1–C2	1.386(3)
N2a–C5	1.458(4)
N2b–C5	1.435(12)
N3a–C8	1.454(4)
N3b–C8	1.434(12)
Bond angles	
C1–S1–C7	88.82(11)
C1–N1–C2	109.7(2)
N3a–N2a–C5	110.8(2)
N3b–N2b–C5	104.4(9)
N2a–N3a–C8	111.1(2)
N2b–N3b–C8	105.3(9)

Table 3
General and crystal data and summary of intensity data collection and structure refinement for compound **2**.

Formula	$C_{17}H_{11}N_3OS$	
M_r	305.36	
Crystal system, colour and habit	Monoclinic, red, irregular block	
Space group	$P\,2_1/n$	
Crystal dimensions (mm)	0.42 × 0.31 × 0.28	
Unit cell parameters:	296 K data	100 K data
a (Å)	5.98360(7)	5.9863(2)
b (Å)	12.41078(14)	12.2048(3)
c (Å)	19.1421(2)	18.9423(6)
β/o	96.3099(11)	97.375(3)
V (Å^3)	1412.90(10)	1372.50(7)
Z	4	4
D_c (gcm^{-3})	1.435	1.478
μ (mm^{-1})	2.075	2.136
F(000)	632	632
2θ range for data collection (o)	4.25–72.46	4.32–72.43
h,k,l range	−7 to 7; −15 to 15; −23 to 19	−7 to 6; −14 to 14; −23 to 22
No. measured reflections	7513	6167
No. independent reflections (R_{int})	2772 (0.0232)	2670 (0.0252)
No. refined parameters	203	203
No. observed reflections, $I \geq 2\sigma(I)$	2432	2553
g_1, g_2 in w	0.0876, 0.2037	0.0790, 0.7079
R, wR [$I \geq 2\sigma(I)$]	0.0434, 0.1362	0.0425, 0.1218
R, wR [all data]	0.0485, 0.1307	0.0437, 0.1205
Goodness of fit on F^2, S	1.047	1.021
Max., min. electron-density (e Å^{-3})	0.253, −0.216	0.333, −0.332
Maximum Δ/σ	<0.001	0.001

Table 4
Selected interatomic distances (Å) and valence and torsion angles (°) for the compound **2**.

Selected bond distances		
	296 K	100 K
N2–N3	1.2957(19)	1.3008(18)
S1–C7	1.7280(17)	1.7349(16)
S1–C1	1.739(2)	1.7422(18)
N3–C8	1.359(2)	1.351(2)
N1–C1	1.285(3)	1.291(2)
N1–C2	1.390(2)	1.392(2)
N2–C5	1.403(2)	1.406(2)
O1–C9	1.289(3)	1.278(2)
Selected angles		
	296 K	100 K
C7–S1–C1	88.93(8)	88.88(8)
C1–N1–C2	109.75(15)	109.94(14)
N3–N2–C5	119.92(14)	120.84(14)
N2–N3–C8	116.86(14)	116.73(14)
C6–C5–N2–N3	4.6(2)	4.3(2)
C9–C8–N3–N2	−0.3(2)	−0.5(2)

Table 5
Hydrogen bond geometry (Å, °) for compounds **1** and **2**.

D–H···A	D–H	H···A	D···A	<D–H···A	Symmetry code
1					
C1–H1···N1	0.930	2.520	3.336(3)	146	1−x,−y,−z
2 (296 K)					
N2–H12N···O1	1.14(4)	1.49(4)	2.520(2)	147(3)	–
C1–H1···N1	0.9300	2.5600	3.329(3)	140.00	4−x,1−y,−z
C4–H4···O1	0.9300	2.5700	3.409(3)	151.00	2−x,−y,−z
2 (100 K)					
N2–H12N···O1	0.98(3)	1.66(3)	2.5148(18)	144(3)	–
C1–H1···N1	0.9300	2.530	3.288(2)	139	4−x,1−y,−z
C4–H4···O1	0.9300	2.530	3.361(2)	149	2−x,−y,−z

a small electron-density (0.30 e/Å^3) at distance N2–H12N 1.13(4) Å and refined freely (U_{iso} (H12N) = 0.131). This is unequivocall confirmation that the hydrazone tautomeric form is present at room temperature (Scheme 2). The low temperature X-ray diffraction study also exhibits that compound **2** exists as hydrazone tautomer with the parameters: N2–H12N bond distance of 0.98(3) Å and U_{iso} (H12N) = 0.064.

The molecular structures were drawn by ORTEP-3 [19] and crystal packings were drawn by PLATON [20].

CCDC 669403 for **1** and CCDC 725589 (296 K) and 725 590 (100 K) for **2** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk].

2.3. Computational studies

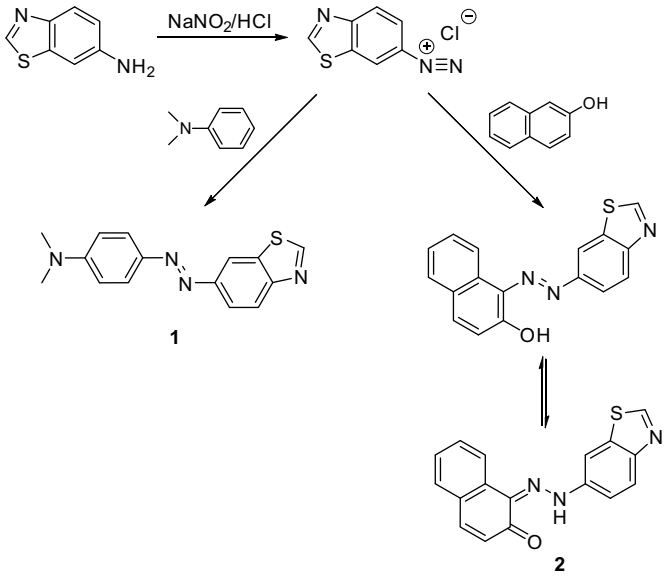
Density functional theory (DFT) hybrid method with the Becke's three-parameter exchange functional and gradient-corrected functional of Lee, Yang and Parr (B3LYP) [21] was employed to predict the equilibrium molecular geometries of two possible tautomers of dye **2**. Both geometries were fully optimized, with tight convergence criteria (Opt = Tight), using following standard basis sets: 6-31G(d), valence double zeta plus polarization functions of d type, and 6-311++G(d,p), valence triple zeta plus diffuse and polarization functions of d and p type. It is generally recognized that for an accurate description of hydrogen bonds at least double zeta quality basis augmented with a set of polarization and diffuse functions set is needed. Therefore a somewhat better geometry description is expected with 6–311++G(d,p) standard basis set. Both minima were verified by establishing that the matrix of energy second derivatives (Hessian) has only positive eigenvalues (all vibrational frequencies real). Gibbs free energy values, which were calculated at the same levels of theory within the harmonic approximation, were used for the evaluation of the tautomeric equilibrium constants.

All calculations were carried out with the *Gaussian 03* program [22].

3. Results and discussion

3.1. Synthesis

The azobenzothiazolyl dyes **1** and **2** were prepared by coupling *N,N*-dimethylaniline and 2-naphthol with diazotized 6-aminobenzothiazole (Scheme 1). *N,N*-dimethylaniline was coupled at pH 5-6 and the pure product **1** was isolated after chromatography on silica in moderate yield of 46%. Dye **1** was reported earlier in order to study its carcinogenicity in comparison with a series of *N,N*-dimethylaminoazobenzene such as methyl yellow, but without experimental details or analytical data [23]. Coupling reaction for compound **2** was performed in basic condition and the pure product was isolated after crystallization from xylene in a good yield of 63%. The structure of these dyes was verified by elemental analysis and by spectroscopic methods (FT-IR, ^{1}H and ^{13}C NMR). The data from NMR spectra taken in DMSO strongly suggest existing of hydrazone form of dye **2** in DMSO solution. The ^{1}H NMR shift at 15.61 ppm assigned to N–H proton is in accordance with literature data for shift found for ^{1}H NMR signal of N–H proton at 16.42 ppm in azo dyes derived from anthranilic acid and 2-naphthol [24]. The crystals suitable for X-ray analysis were obtained for **1** by slow evaporation from dichloromethane–petrolether mixture (1:1), and for **2** by slow evaporation of chloroform–ether mixture (1:1), respectively.



Scheme 1. Synthesis of azo dyes **1** and **2**.

3.2. Crystal structure study

The molecular structure of 6-(4-*N*,*N*-dimethylaminophenylazo)benzothiazole (**1**) is depicted in Fig. 1 and the crystal structure in Fig. 2a and b. The molecular and crystal structure of 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole (**2**) is depicted in Fig. 3a (room temperature data; $T = 296$ K) and Fig. 3b (data at $T = 100$ K) and in Fig. 4a and b, respectively.

The positional disorder of the azo group in molecule **1** has been resolved to 9:1 distribution of major and minor component, so Fig. 1 reveals only the major component. Both molecules **1** (with exclusion of the hydrogen atoms, which belong to methyl groups) and **2** are almost planar in the crystalline state exhibiting highly delocalized π-electron systems. The dihedral angle between two aromatic rings defined by the atoms C8–C13 and C2–C7, S1, N1 in **1** and by the atoms C8–C17 and C2–C7, S1, N1 in **2** amounts 5.46(9)° and 5.90(11)°, respectively. The position of the substituents attached to the azo linkage is *trans* relative to each other, so the configuration of the molecule is *E* in the crystalline state in **1**. The torsion angles along the central N–N moiety confirm *trans* configuration in **1** with the value of −179.8(2)° for the angles C5–N2a–N3a–C8 in **1**. The geometry within the benzothiazole rings in both **1** and **2** is in accordance with the literature data [25]. The azo linkage bond distance of the major component N2a = N3a in **1** and N2–N3 bond distance in **2** amount 1.224(3) and 1.296(2) Å (1.301(2) Å at $T = 100$ K), respectively (Tables 2 and 4). The average N=N bond distance for the structural fragment C_{Ar}–N=N–C_{Ar} amounts 1.255 Å [25]. The N=N double bond in such fragments amounts 1.222 Å and 1.245 Å, for *trans* and *cis* configuration, respectively. The value of N=N bond distance in **1** resembles the same bonds in 4-*N*,*N*-dimethylaminophenylazo derivatives and amounts 1.24 Å in *p*-dimethylaminoazobenzene [24,26], 1.261(6) Å in 1-phenyl-4-(*N*,*N*-dimethylamine)-phenyl [27], 1.258(6) Å in 4′-(dimethylamino)-4-nitroazobenzene [28], 1.264 and 1.266 Å in 4-[(2-methoxy-4-nitro-phenylazo)-phenyl]-dimethyl-amine [29], 1.263(2) Å in 4′-(dimethylamino)-2-nitroazobenzene [30], 1.271(4) Å in 2-trifluoromethyl-4′-dimethylaminoazobenzene [31] and 1.254(2) Å in 2′,6′-dichloro-4-dimethylaminoazobenzene [32]. The short N=N bond distance value in compound **1** (with the central structural fragment C_{Ar}–N=N–C_{Ar}) is as expected and in correlation with neighbouring N–Csp^2 bonds [C8–N3a of 1.454(4) Å and C5–N2a of 1.458(4) Å] falling in the range 1.41–1.46 Å for N–Csp^2 bonds which are dominantly σ in character (Table 2).

Compound **2** contains an –OH group in an *ortho*-position to the azo linkage which enable intramolecular hydrogen bond formation of the O–H···N or N–H···O type due to the presence of two possible tautomeric forms, the azo and the hydrazone (Scheme 2). The presence of one or another tautomer (or the mixture of both) can be concluded on the basis of the main structural features in the central fragment of the molecule regarding N–N, C_{Ar}–O and Csp^2–N bonds and by hydrogen atom position [33,34]. Variable-temperature X-ray crystallography can be used for detection of dynamic disorder in the N–H···O ↔ O–H···N system. The hydrogen atom location at the nitrogen or oxygen site in compound **2** is determined by the survey of difference Fourier map at the final stages of crystallographic refinement. The existence of the hydrazone form is unequivocally established (N2-H12N 1.14(4) Å for 296 K structure of 2 and 0.98(3) Å for 100 K structure) (Tables 4 and 5, Scheme 2). The longer N–N bond value in compound **2** indicates the presence of hydrazone tautomer (the mean value for the pure Nsp^2–Nsp^2 single bond is 1.401 Å). The Csp^2–O bond distance of 1.289(3) Å and 1.278(2) Å at $T = 296$ and 100 K, respectively, (Csp^2–OH in phenol is 1.362 Å and keto bond is 1.210 Å [23]) can indicate partial double bond character due to the intramolecular hydrogen bond formation. The bond distance values of C8–N3 (1.359(2) Å) and C5–N2 (1.403(2) Å) in compound **2** confirm conjugation. The analogous trend of one shorter N–Csp^2 bond and one dominantly σ N–Csp^2 bond is not observed in the compound **1** where both N–Csp^2 bonds are dominantly σ in character. The geometry of the central highly conjugated system in **2** is comparable with that found in 1-(phenylazo)-2-naphthol [10,35], which is averaged "X-ray structure" of both tautomeric forms (the corresponding bond distances: N–N of 1.308(4) Å, C–O of 1.261(4) Å, C–N 1.338(4) and 1.406(4) Å).

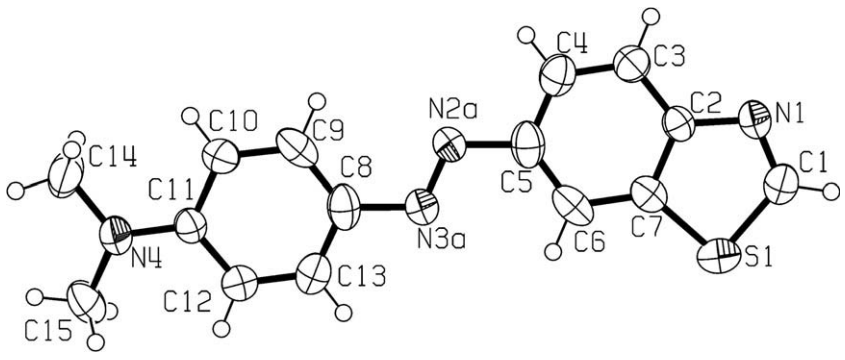


Fig. 1. ORTEP drawing of 6-(4-*N*,*N*-dimethylaminophenylazo)benzothiazole (1) with the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level at 293 K.

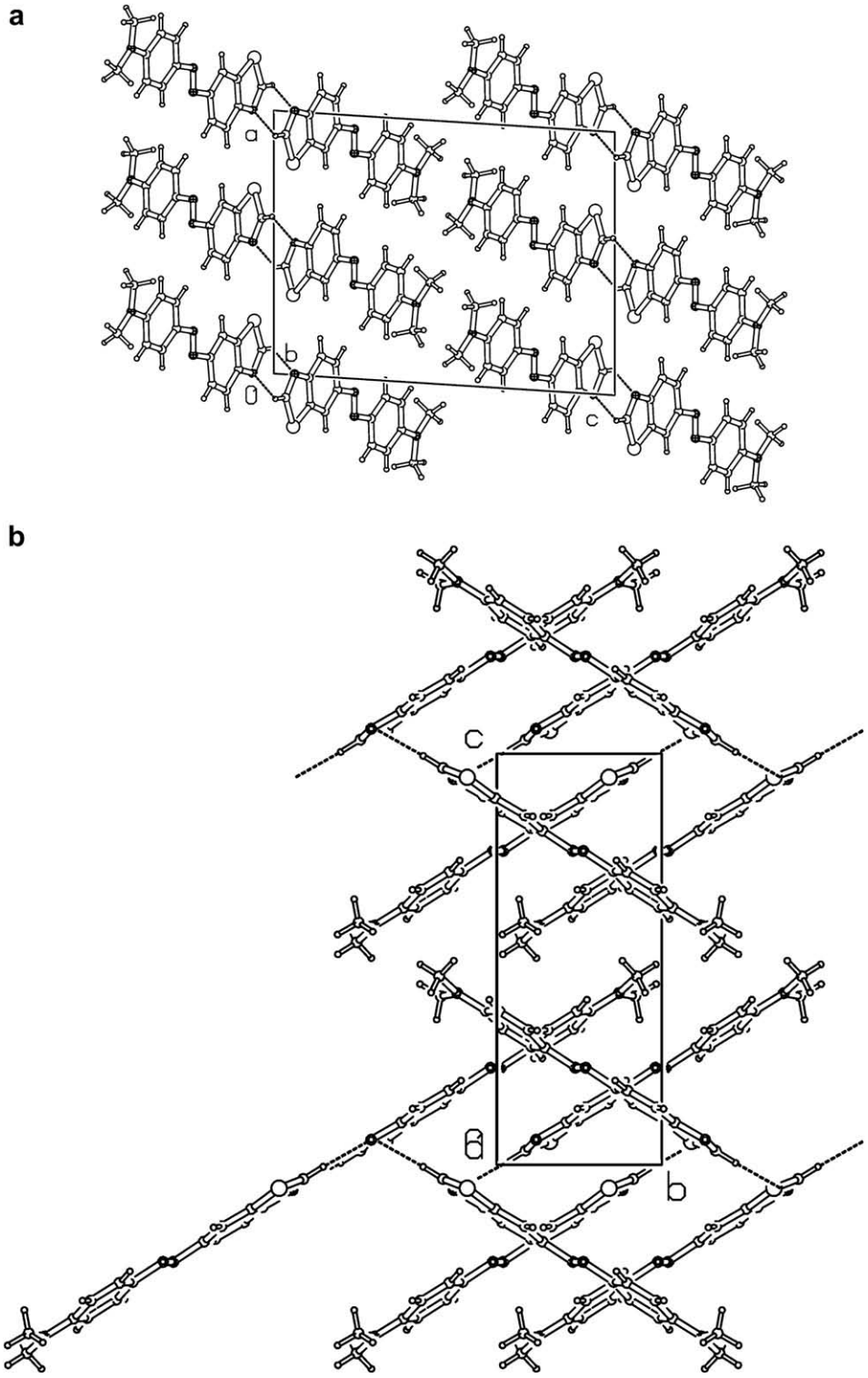


Fig. 2. a. Crystal structure of 6-(4-*N*,*N*-dimethylaminophenylazo)benzothiazole (1) viewed along *y* axis. Hydrogen bond of the C–H···N type is shown as dashed line forming discrete dimers. b. Crystal structure of 6-(4-*N*,*N*-dimethylaminophenylazo)benzothiazole (1) viewed along *x* axis. The dimers are assembled into herringbone-fashion.

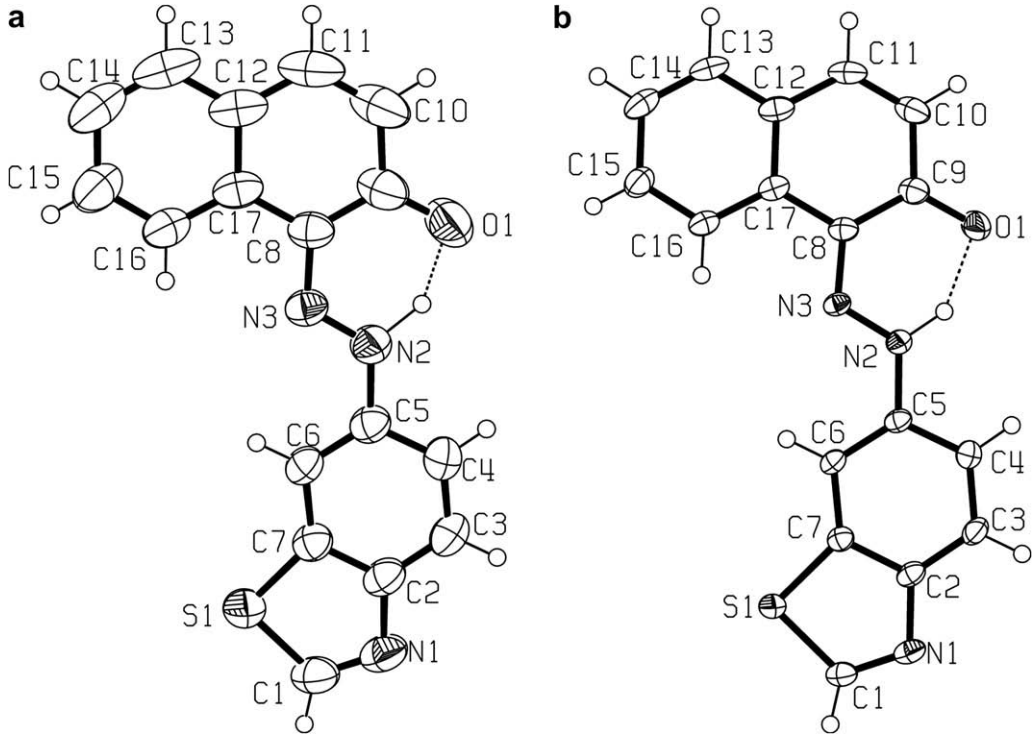


Fig. 3. ORTEP drawing of 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole, (2), with the numbering scheme. The thermal ellipsoids are drawn at the 50% probability level at 293 K.

Kelemen and co-authors established that the bond range for the N═N bond in azo tautomer is 1.20–1.28 Å [36]. On the basis of these geometries one can conclude that compound **2** at 100 K is mainly (but not exclusively), hydrazone pigment.

The intramolecular hydrogen bond N2–H12N···O1 which forms pseudoaromatic six-membered ring and preserves planarity of that part of the molecule (inhibiting rotation around C8–N3 bond) belongs to the class of resonance-assisted hydrogen bond (RAHB) which is particularly short (2.520(2) Å). This value is in accordance with the N···O distance range found in analogous compounds (2.50–2.55 Å) [37]. By the intermolecular hydrogen bond of the C–H···N type between thiazolyl C–H group and thiazolyl nitrogen atom [C1–H1···N1^{i}; i = 1−x,−y,−z; C1–H1 0.9300 Å; H1···N1 2.520 Å; C1···N1 3.336(3) Å; <C1–H1···N1 146°] (Table 5) the six-membered

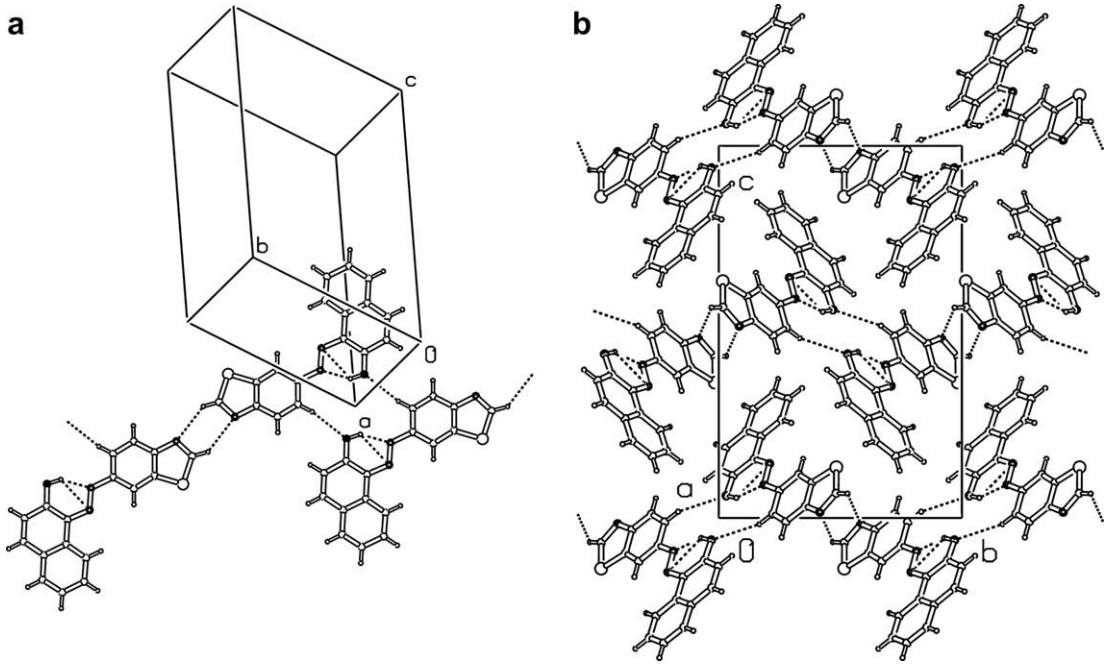
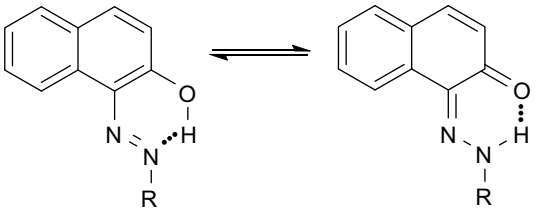


Fig. 4. a. Crystal structure of 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole, (2), with the hydrogen bond motifs. Hydrogen bonds are shown as dashed lines. b. Crystal structure of 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole, (2), viewed along *x* axis.



Scheme 2. Tautomerization in β-naphthol monoazo derivatives.

centrosymmetric rings connecting pairs of neighbouring molecules into discrete dimers in **1** is obtained. The dimers are assembled into a herringbone-fashion in a *bc* plane. The shortest distance found between centroids of aromatic ring amounts 3.855 Å between phenyl rings defined by the atoms C2–C7 and C8–C13.

The dihedral angle between these two rings amounts 5.29°. According to such geometry, π···π interactions between phenyl rings of benzothyazolyl part of molecule in the crystalline state can be established. The analogous intermolecular hydrogen bond exists in compound **2** with the similar hydrogen bond geometry (Table 5). Moreover, there is a weak intermolecular hydrogen bond of the C–H···O type (Table 5) in **2** forming 3D hydrogen bonded network. There is no evidence for π···π interactions in **2**.

3.3. Computational results

DFT calculations have been performed for the two tautomers of compound **2**. Optimized molecular structures of azo and hydrazone tautomers are depicted in Fig. 5a and b, respectively. Their calculated energies and relative energies are presented in Table 6. The hydrazone tautomer is more stable than azo tautomer by 10.42 and 4.18 kJ mol^{-1} at B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) levels of theory, respectively.

The energy difference is in accordance with the literature data of similar compounds obtained at B3LYP/6-31 + G(d,p) level of theory [35,37]. These calculations have shown larger stability of hydrazone tautomers over azo tautomers for phenyl-substituted 1-arylazo-naphthalen-2-ols with *p*-NO_2, *m*-OCH_3, *p*-Cl and *p*-F groups by 6.65, 5.27, 3.81 and 1.67 kJ mol^{-1}, respectively. The similar position of tautomeric equilibrium has been calculated for nonsubstituted 1-phenylazo-naphthalen-2-ol (4.64 kJ mol^{-1}). The reverse tautomeric equilibrium has been determined only for 1-arylazo-naphthalen-2-ols with strong electron-donating groups such as *p*-$N(CH_3)_2$ and *p*–O^- for which azo tautomers are more stable than hydrazone tautomers by 2.05 and 5.61 kJ mol^{-1}, respectively.

The tautomeric equilibrium constants, K_T, between azo and hydrazone tautomer are calculated by using the following equation:

Table 6
Calculated energies (E/hartree[a]), Gibbs free energies (ΔG/hartree[a]) and relative energies (ΔE/kJ mol^{-1}) of the azo and hydrazone tautomeric forms of compound **2**.

B3LYP/6-31G(d)		
	Azo	Hydrazone
E/hartree	−1292.087250	−1292.091220
ΔE/kJ mol^{-1}	10.422	0.000
ΔG/hartree	−1291.888309	−1291.891648
B3LYP/6-311++G(d,p)		
	Azo	Hydrazone
E/hartree	−1292.341447	−1292.343039
ΔE/kJ mol^{-1}	4.180	0.000
ΔG/hartree	−1292.144523	−1292.145860

[a] 1 hartree = 2525.5 kJ mol^{-1}.

$$K_T = e^{-(\Delta\Delta G/RT)}$$

where the gas constant R is 8.3145 10^{-3} kJ mol^{-1} K^{-1} and the temperatures T are 296 and 100 K [38–40]. The quantity $\Delta\Delta G$ is the difference between the Gibbs free energies of the given tautomers which are shown in Table 6: $\Delta\Delta G = \Delta G$(hydrazone) – ΔG(azo). $\Delta\Delta G$ values are −8.79 kJ mol^{-1} and −3.52 kJ mol^{-1} at B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) levels, respectively. The tautomeric equilibrium constants, K_T, at both temperatures are shown in Table 7. The mole fractions of individual tautomer are calculated by using following equations [41]:

$$N_{azo} = \frac{1}{1+K_T} \quad N_{hydrazone} = \frac{K_T}{1+K_T}$$

which give more than 80% of hydrazone form at the room temperature, and more than 98% at 100 K at both levels of theory. Table 8 provides DFT results for selected interatomic distances and angles of the two tautomeric forms. Whereas the two used basis sets, 6-31G(d) and 6-311++G(d,p), showed little differences in geometry parameters, only later basis set geometry results are shown.

Both tautomers are planar (in the C_s point group). Major variation in geometry of azo and hydrazone forms are at N2–N3, N3–C8 and O1–C9 bonds and hydrogen bonds at N2 and O1 atoms (N2–H and O1–H). The remainder of the bonds and angles in azo as well as hydrazone form do not change significantly. N2–N3 bond distances in azo and hydrazone tautomer are 1.272 Å, indicating more double bond character, and 1.306 Å, indicating more single bond character, respectively. According to the single-crystal structure distance of 1.296 and 1.301 Å at 296 and 100 K, respectively (Table 4), predominance of the hydrazone tautomer is confirmed. According to the N3–C8 and O1–C9 calculated and single-crystal bond distances, the preference of any tautomer could not be concluded. On the other hand, hydrogen bond distances are 1.662 and 1.001 Å

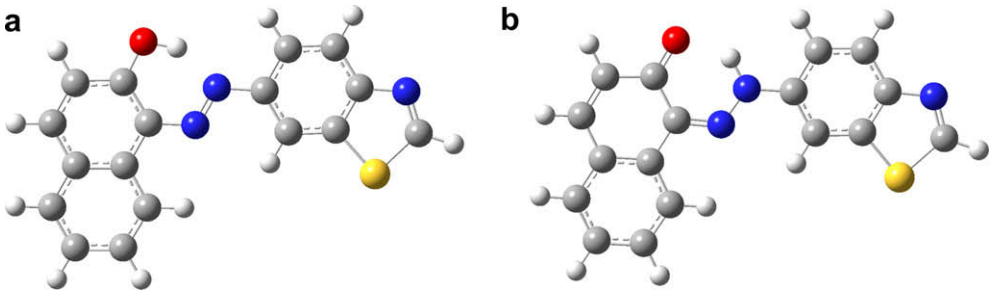


Fig. 5. a. Azo tautomer optimized structure of 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole, **2**, at B3LYP/6-311++G(d,p) level of theory. b. Hydrazone-tautomer optimized structure of 6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole, **2**, at B3LYP/6-311++G(d,p) level of theory.

Table 7
Calculated tautomeric equilibrium constants (K_T) and mole fractions of the azo and hydrazone tautomeric forms (N_{azo} and $N_{hydrazone}$) of compound **2** at 296 and 100 K.

B3LYP/6-31G(d)		
	296 K	100 K
K_T	35.23	37,931.34
N_{azo}	0.0276	0.0000
$N_{hydrazone}$	0.9724	1.0000
B3LYP/6-311++G(d,p)		
	296 K	100 K
K_T	4.17	68.54
N_{azo}	0.1934	0.0144
$N_{hydrazone}$	0.8066	0.9856

Table 8
Selected interatomic distances (Å) and valence and torsion angles (°) for the azo and hydrazone tautomeric forms of compound **2** calculated at B3LYP/6-311++G(d,p) level of theory.

Selected bond distances		
	Azo	Hydrazone
N2–N3	1.2716	1.3055
S1–C7	1.7542	1.7518
S1–C1	1.7645	1.7672
N3–C8	1.3823	1.3247
N1–C1	1.2889	1.2880
N1–C2	1.3842	1.3846
N2–C5	1.4110	1.4005
O1–C9	1.3333	1.2512
N2–H	1.6615	1.0346
O1–H	1.0007	1.7118
O1–N2	2.5457	2.5594
Selected angles		
	Azo	Hydrazone
C7–S1–C1	88.17	88.23
C1–N1–C2	110.73	110.76
N3–N2–C5	116.58	121.71
N2–N3–C8	117.27	120.03
O1–H–N2	144.84	136.05
C6–C5–N2–N3	0.00	0.00
C9–C8–N3–N2	0.00	0.00

for N2–H and O1–H bonds, respectively, in azo tautomer, and 1.035 and 1.712 Å for N2–H and O1–H bonds, respectively, in hydrazone tautomer. In the crystal structure (Table 5), N2–H and O1–H distances are 1.14(4) and 1.49(4) Å, at 296 K, and 0.98(3) and 1.66(3) Å at 100 K, respectively. It is obvious that crystal structural parameters which have been commented agree better with calculated ones for the hydrazone tautomer and overall matching is better at the lower temperature, indicating shifting in tautomeric equilibrium towards the hydrazone form.

4. Conclusion

The synthesis, FT-IR, ^{1}H and ^{13}C NMR, crystal and molecular structure determined by single-crystal X-ray diffraction as well as DFT quantum-chemical calculations, of two dyes derived from 6-aminobenzothiazole: (6-[(4-*N*,*N*-dimethylaminophenyl)diazenyl]-benzothiazole) (**1**) and (6-[(2-hydroxy-1-naphthyl)diazenyl]benzothiazole (**2**) are reported. The single-crystal X-ray study resolved the presence of two configurations with an approximately 9:1 weighting within asymmetric unit of **1** (disorder of azo linkage). Since compound **2** could exist in two tautomeric forms depending on hydrogen population on either the oxygen or nitrogen site, the X-ray crystallographic study at two different temperatures (296 and 100 K) and DFT quantum-chemical calculations have been performed in order to unequivocally established the tautomer adopts by compound **2**. Therefore, tautomeric equilibrium constants and mole fractions of individual tautomer of compound **2** at 296 and 100 K are calculated.

Both molecules **1** and **2** are highly delocalized π-electron systems, which result in an essentially planar structures (excluding methyl groups in **1**). Compound **1** prefers a 100% *E*-configuration due to the substituents positions attached to central azo linkage. For compound **2** the predominance of the hydrazone tautomer over the azo at both temperatures (more than 80% at the 296 K and more than 98% at 100 K) and the existence of the intramolecular RAHB (resonance-assisted hydrogen bond) of the N–H···O type are confirmed. The intermolecular hydrogen bonds of the C–H···N type exist in crystal structure of **1** and **2**, while in **2** there are additional C–H···O bonds.

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References

[1] Zollinger H. Color chemistry: syntheses, properties and application of organic dyes and pigments. 2nd ed. Weinheim: VCH; 1991.
[2] Gregory P. In: Hunger K, editor. Industrial dyes: chemistry, properties and applications. Weinheim: Wiley-VCH; 2002. p. 543–85.
[3] Clark RJH, Hester RE. Advances in materials science spectroscopy. New York: John Wiley & Sons; 1991.
[4] Towns AD. Developments in azo disperse dyes derived from heterocyclic diazo components. Dyes and Pigments 1999;42:3–28.
[5] Freeman HS. Color yes, toxicity no: systematic approaches to meeting this challenge. AATCC Review 2004;4:16–21.
[6] Humphreys M, Hall N, Phillips DAS, Taylor JA. Synthesis and application of disperse dyes based on 1,4-bis(benzothiazol-2-yl)benzene to polyethylene terephtalate. Dyes and Pigments 2003;59:193–200.
[7] Christie RM, Morgan KM, Islam S. Molecular design and synthesis of *N*-aryl-sulfonated coumarin fluorescent dyes and their application to textiles. Dyes and Pigments 2008;76:741–7.
[8] Hunger K. The effect of crystal structure on colour application properties of organic pigments. Review of Progress in Coloration and Related Topics 1999;29:71–84.
[9] McGeorge G, Harris RK, Batsanov AS, Churakov AV, Chippendale AM, Bullock JF, et al. Analysis of a solid-state conformational rearrangement using ^{15}N NMR and X-ray crystallography. Journal of Physical Chemistry A 1998;102:3505–13.
[10] Olivieri AC, Wilson RB, Paul IC, Curtin DY. ^{13}C and X-ray structure determination of 1-(arylazo)-2-naphthols. Intramolecular proton transfer between nitrogen and oxygen atoms in the solid state. Journal of the American Chemical Society 1989;111:5525–32.
[11] Özen AS, Doruker P, Aviyente V. Effect of cooperative hydrogen bonding in azo-hydrazone tautomerism of azo dyes. Journal of Physical Chemistry A 2007;111:13506–14.
[12] Racané L, Tralić-Kulenović V, Mihalić Z, Pavlović G, Karminski-Zamola G. Synthesis of new amidino-substituted 2-aminothiophenoles: mild basic ring opening of benzothiazole. Tetrahedron 2008;51:11594–602.
[13] Racané L, Tralić-Kulenović V, Kitson R, Karminski-Zamola G. Synthesis and "in vitro" antiproliferative activity of new cyano and amidino substituted 2-phenyl-benzothiazoles. Monatshefte fur Chemie 2006;137:1571–7.
[14] Tralić-Kulenović V, Racané L, Karminski-Zamola G. Absorptions and fluorescence properties of some substituted 2-furylbenzothiazoles and their vinylogues in different solvents. Spectroscopy Letters 2003;36:43–50.
[15] Tralić-Kulenović V, Fišer-Jakić L. Solvent and substituent effect on the absorption and fluorescence properties of substituted 2-phenylbenzothiazoles and their vinylogues. Spectrochimica Acta Part A 1997;53:271–3.
[16] Boggust WA, Cocker W. Experiments in the chemistry of benzothiazole. Journal of the Chemical Society 1949:355–62.
[17] Oxford Diffraction. Xcalibur CCD system, CrysAlis software system, versions 1.171.31. & 1.171.32.29. Abingdon; Oxfordshire, England: Oxford Diffraction Ltd.; 2006.
[18] Sheldrick GM. A short history of SHELX. Acta Crystallographica 2008;A64:112–22.
[19] Farrugia LJ. Computer program abstracts, ORTEP-3 for Windows – a version of ORTEP-III with a graphical user interface (GUI). Journal of Applied Crystallography 2003;32:837–8.

[20] Spek AL. Single-crystal structure validation with the program PLATON. Journal of Applied Crystallography 2003;36:7–13.
[21] Parr RG, Yang W. Density-functional theory of atoms and molecules. Oxford: Oxford Univ. Press; 1989.
[22] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 03, revision C02. Wallingford CT: Gaussian Inc.; 2004.
[23] Ashby J, Callander RD, Lefevre PA, Paton D, Fishwick B. Mutagenicity to *Salmonella* of the *mono*methylamino and *N*-cyanoethyl analogues of 4-dimethylaminoazobenzene (DAB) and 6-dimethylaminophenylazobenzthiazole (6BT). Mutation Research 1984;128:11–6.
[24] Lyčka A, Luštinec D, Holeček J, Nádvorník M, Holčapek M. ^{27}Al, ^{15}N, ^{13}C and ^{1}H NMR spectra and negative-ion electrospray mass spectra of the 2:1 aluminium(III) complexes of azo dyes derived from anthranilic acid. Dyes and Pigments 2001;50:203–9.
[25] Allen FH, Kennard O, Watson DG, Brammer L, Orpen AG. Journal of the Chemical Society Perkin Transactions II 1987:S1–19.
[26] Coiro VM, Giglio E, Mazza F, Pavel NV, Pochetti G. Structure of the 4:1 inclusion compound between deoxycholic acid and (*E*)-*p*-dimethylaminoazobenzene. Acta Crystallographica 1982;B38:2615–20.
[27] Whitaker A. Crystal and molecular structure of C.I. Solvent Yellow 2, 1-phenylazo-4 (N, N-dimethylamine)-phenyl. Journal of Crystallographic and Spectroscopic Research 1992;22:151–5.
[28] Adams H, Allen RWK, Chin J, O'Sullivan B, Styring P, Sutton LR. 4′-(Dimethylamino)-4-nitroazobenzene. Acta Crystallographica 2004;E60:o289–90.
[29] Yang W, You X-L, Zhong Y, Zhang D-Ch. The crystal structure of 4-[(2-methoxy-4-nitro-phenylazo)-phenyl]dimethylamine. Dyes and Pigments 2007;73:317–21.
[30] Zhang D-Ch, Ge L-Q, Fei Zh-H, Zhang Y-Q, Yu K-B. 4′-(Dimethylamino)-2-nitroazobenzene. Acta Crystallographica 1998;C54:1909–11.
[31] Sasaki C, Kitoh S, Yamada K, Kunimoto K-K, Maeda S, Kuwae A, et al. Crystal structure of 2-trifluoromethyl-4′-dimethylaminoazobenzene. Analytical Sciences 2003;19:x1–2.
[32] Yang W, You XL, Zhang Y, Zhang D-Ch. The crystal structure of 2′,6′-dichloro-4-dimethylaminoazobenzene. Dyes and Pigments 2006;68:27–31.
[33] Zen AS, Doruker P, Aviyenete V. Effect of cooperative hydrogen bonding in azo–hydrazone tautomerism of azo dyes. Journal of Physical Chemistry A 2007;111:13506–14.
[34] Schmidt MU, Brüning J, Wirth D, Bolte M. Two azo pigments based on β-naphthol. Acta Crystallographica 2008;C64:o474–7.
[35] Gilli 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 system. A variable-temperature X-ray crystallographic and DFT computational study. Journal of the American Chemical Society 2002;124:13554–67.
[36] Kelemen J, Kormany G, Rihs G. Azo–hydrazone tautomerism in azo dyes. III. The tautomeric structure of 1-(4′-nitrophenylazo)-2-naphthylamine from crystal structure determination. Dyes and Pigments 1982;3:249–71.
[37] Gilli P, Bertolasi V, Pretto L, Antonov L, Gilli G. Variable temperature X-ray crystallographic and DFT computational study of the N–H···O/O–H···N tautomeric comeptition in 1-(arylazo)-2-naphthols. Outline of a transition state hydrogen bond theory. Journal of the American Chemical Society 2005;127:4943–53.
[38] He L, El-Shafei A, Freeman HS, Boyle P. X-ray and molecular modelling studies of 4-[N-alkylamino]azobenzene dyes. Dyes and Pigments 2009;82:299–306.
[39] Mazurek AP, Sadlej-Sosnowska N. Studies on tautomerism in tetrazole: comparison of Hartree-Fock and density functional theory quantum chemical methods. Chemical Physics Letters 2000;330:212–8.
[40] Oziminski WP, Dobrowolski JC, Mazureka AP. DFT studies on tautomerism of C5-substituted 1,2,4-triazoles. Journal of Moleculare Structure: Theochem 2004;680:107–15.
[41] Hür D, Güven A. The acidities of some indoles. Journal of Moleculare Structure: Theochem 2002;583:1–18.