Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 74 (2007) 531–535
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Synthesis, spectral characterization and crystal structure of 4-(4,5-dicyano-1-*H*-imidazolyazo)-*N*,*N*-diethylaniline

Yongfang Zhang, Guoqi Zhang, Quan Gan, Shuangqing Wang*,
Huijun Xu, Guoqiang Yang*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, China

Received 17 October 2005; received in revised form 18 January 2006; accepted 15 March 2006
Available online 26 May 2006

Abstract

The synthesis, crystal structure analysis and characterization of 4-(4,5-dicyano-1-*H*-imidazolyazo)-*N*,*N*-diethylaniline ($C_{15}H_{15}N_7$, DIAA) were reported. Both the effects of pH value and solvent polarity upon the absorption properties of the compound were presented. The compound DIAA is monoclinic in $C2/c$ with $a = 20.793(4)$ Å, $b = 14.008(3)$ Å, $c = 15.771(3)$ Å, $\beta = 102.79(3)°$, $V = 4479.6(15)$ Å^3, $D_{calc} = 1.143$ g/cm^3 and $Z = 8$. Crystal stacking scheme indicates the hydrogen bonds and intermolecular $\pi \cdots \pi$ stacking interactions; the azo molecules arrange in a head-to-tail fashion along the *ac* plane due to the strong 'push–pull' electron system.

Keywords: Monoazo; Crystal structure; Solvent effect

1. Introduction

Azo dyes have attracted considerable attention due to their versatile application in various fields. Their importance in dye industry, in biological chemistry, and in many high-technological frontier applications has been documented over years [1–5]. Recently, the study of azo dyes as nonlinear optical materials manifested that many heterocyclic azo dyes showed large molecular hyperpolarizabilities [6–8]. Such optical properties depended on not only the spectroscopic properties of the molecules, but also their crystallographic arrangement [9–11].

In this paper, a monoazo dye 4-(4,5-dicyano-1-*H*-imidazolyazo)-*N*,*N*-diethylaniline (DIAA) was synthesized; the single-crystal X-ray diffraction and its crystal packing were presented. Both the effects of varying pH values and solvent polarity upon the absorption properties of the compound were also investigated. These properties are very important for the practical applications of such monoazo compounds as the precursors of nonlinear optical materials.

2. Experimental

The starting materials were purchased from ACROS Organic or TCI Co. Ltd. and used without further purification unless otherwise specified. Solvents for spectral measurements were of spectrophotometric grade.

2.1. Preparation

The monoazo dye DIAA was readily synthesized in high yield according to the following methods [12–14].

Diazotization reaction: 1.064 g (0.008 mol) of 2-amino-4,5-dicyano-1-*H*-imidazole was dissolved in 25.6 ml water and 2.6 ml concentrated hydrochloric acid, and then cooled to 0–5 °C in an ice-brine bath. Solid sodium nitrite (0.600 g, 0.0087 mol, 10% excess) was added to the above solution over 30 min while the temperature was maintained at

---

* Corresponding authors. Tel.: +86 10 82617263; fax: +86 10 82617315.
E-mail addresses: g1704@iccas.ac.cn, gqyang@iccas.ac.cn (G. Yang).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.03.011

0–5 °C, and stirring was continued for 1 h. Urea (240 mg) was then added to destroy the excess nitrous acid.

Coupling reaction: 1.192 g (0.008 mol) of *N*,*N*-diethylaniline was dissolved in 15 ml of acetic acid and cooled to 0–5 °C in an ice-brine bath. The solution was then slowly added to the vigorously stirred diazonium salt solution. The mixture was then stirred for 5 h. Sodium acetate (6 g) was added to adjust the pH value to 4. Water (50 ml) was added dropwise subsequently, and it was stirred for another 3 h. The solution was left to stand overnight while the temperature rose spontaneously to room temperature. The orange precipitate was collected and washed thoroughly with cold water and dried. Crude dye (2.030 g) was obtained. The yield was about 86.6%. The azo dye was recrystallized twice from methanol. Block-like deep red crystal was grown from ethanol by slow evaporation at ambient temperature for two weeks.

MALDI-TOF-MS ($C_{15}H_{15}N_7$) *m/z*: 294 $[M+1]^+$, 316 $[M+Na]^+$.

Anal. Calcd. for $C_{15}H_{15}N_7$ (293): C, 61.43; H, 5.12; N, 33.45. Found: C, 61.07; H, 5.45; N, 33.31.

IR (KBr, cm^{-1}): 2988, 2930 (w, $-CH_2CH_3$), 2235 (m, −CN), 1601 (s, Benz. ring), 1544 (w, Imidazole, −C=C/−C=N), 1343, 1272 (s, C−N=N−C,−C−N), 1175, 1155 (m,$-N(CH_2CH_3)_2$, −C−N), 834 (w, Benz. ring).

^1H NMR (d_6-DMSO as solvent), δ (ppm): 1.13 (t, 6H); 3.52 (q, 4H); 6.87 (d, 2H); 7.82 (d, 2H); 3.98 (s, 1H).

A general ORTEP structure view and atom labeling scheme for DIAA molecule is shown in Fig. 1. DIAA is a planar molecule and the distortion from planarity is small (see the structure analysis below).

2.2. Instruments and methods

MALDI-TOF-MS measurements were carried out on a Brucker APEX II and KYKY-ZHP-5 spectrometer. FT-IR spectra were recorded in the solid state over the range 4000–400 cm^{-1} using a BIO-RAD FT-165 IR spectrometer. Samples for micro-analyses were dried under vacuum and the analysis was performed with a Carlo Erba-1106 elemental analyzer. ^1H NMR spectra were measured with a Bruker dmx300 MHz NMR spectrometer at room temperature in d_6-DMSO. UV–vis absorption spectra were obtained on a Hitachi UV-3010 spectrophotometer by monitoring the spectra between 350 and 700 nm.

2.3. X-ray crystallography

Crystals suitable for X-ray diffraction studies were obtained by solvent evaporation at 25 °C. Accurate unit cell parameters were determined by a least-square fit of 2θ values, measured for 200 strong reflections, and intensity data sets were measured on Rigarku Raxis Rapid IP diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The intensities were corrected for Lorentz and polarization effects, but no corrections for extinction were made. All structures were solved by direct methods. The crystal data and the correlated parameters are listed in Table 1.

3. Results and discussion

The compound DIAA displayed ordered molecular arrangement in the solid state and significant intermolecular interactions were observed. The compound crystallizes in monoclinic space group *C*2/*c*, each asymmetry unit contains one azo molecule and two crystalline ethanol molecules. The fractional atomic coordinates and equivalent isotropic thermal parameters for nonhydrogen atoms are given in Table 2. The selected bond lengths and angles are listed in Table 3.

The dyeing and photochemical properties of azo dyes are often affected by molecular structures. Besides hydrogen

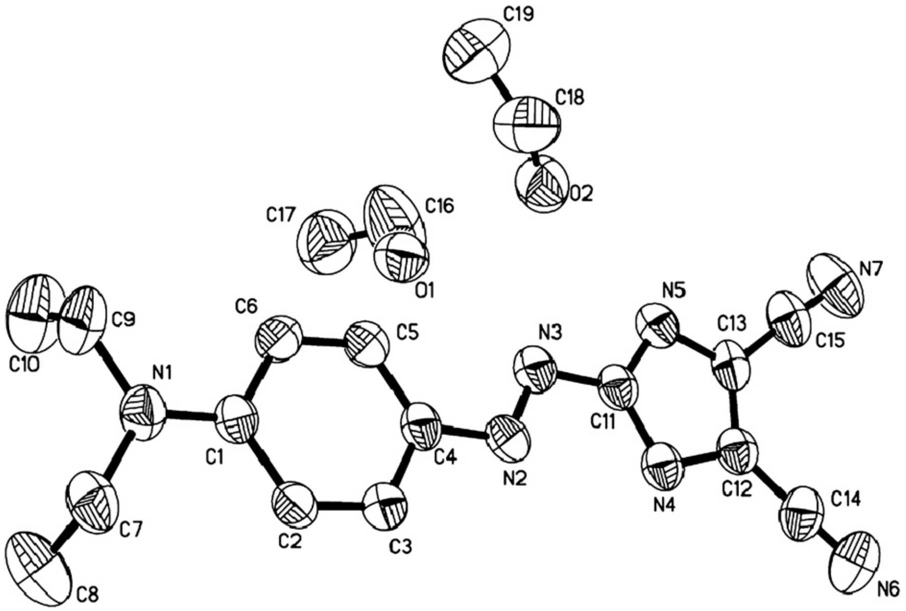

Fig. 1. Molecular structure and atomic numbering of DIAA.

Table 1
Crystal data and structure refinement for DIAA

Compound	$C_{19}H_{27}N_7O_2$
Crystal colour	Deep red
Formula wt.	385.48
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	$a = 20.793(4)$ Å $\alpha = 90°$ $b = 14.008(3)$ Å $\beta = 102.79(3)°$ $c = 15.771(3)$ Å $\gamma = 90°$
Volume (Å^3)	4479.6(15)
Z	8
Density (calculated, g/cm^3)	1.143
F_{000}	1648
Crystal dimensions (mm)	0.52 × 0.43 × 0.26
θ range for data collection (°)	2.07–27.48
Ranges of *h*, *k*, *l*	$-26 \le h \le 26$ $-17 \le k \le 17$ $-19 \le l \le 20$
Reflections collected	Total: 20,110 Unique: 5066 ($R_{\text{int}} = 0.0448$)
Refinement method	Full-matrix least-squares on F^2
Absorption correction	Empirical
Max. and min. transmissions	0.9796 and 0.9606
Data/restraints/parameters	5066/0/254
Goodness-of-fit on F^2	0.988
Final *R* indices ($I > 2\sigma(I)$)	$R1 = 0.0812$, w$R2 = 0.1979$
R indices (all data)	$R1 = 0.2001$, w$R2 = 0.2379$
Extinction coefficient	0.0037(7)
Largest diff. peak and hole e$^-$/Å^3	0.336 and −0.161

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for DIAA

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
N(1)	−2531(1)	−450(2)	−3676(2)	81(1)
N(2)	−131(1)	265(2)	−1345(2)	74(1)
N(3)	212(1)	−436(2)	−1013(2)	75(1)
N(4)	979(1)	788(2)	−248(2)	76(1)
N(5)	1254(1)	−749(2)	−89(2)	79(1)
N(6)	2287(2)	2165(3)	976(2)	125(1)
N(7)	2828(2)	−944(3)	1264(2)	143(2)
C(1)	−1952(1)	−284(2)	−3099(2)	68(1)
C(2)	−1713(1)	640(2)	−2862(2)	72(1)
C(3)	−1124(2)	786(2)	−2311(2)	75(1)
C(4)	−727(1)	22(2)	−1925(2)	69(1)
C(5)	−955(2)	−900(2)	−2142(2)	73(1)
C(6)	−1545(2)	−1051(2)	−2707(2)	76(1)
C(7)	−2959(2)	343(3)	−4066(2)	95(1)
C(8)	−3436(2)	670(4)	−3542(3)	145(2)
C(9)	−2775(2)	−1421(3)	−3912(3)	104(1)
C(10)	−3101(2)	−1860(4)	−3264(3)	147(2)
C(11)	804(2)	−132(3)	−458(2)	71(1)
C(12)	1599(2)	745(3)	294(2)	77(1)
C(13)	1750(2)	−198(3)	382(2)	79(1)
C(14)	1975(2)	1542(3)	673(3)	93(1)
C(15)	2347(2)	−633(3)	875(2)	100(1)
C(16)	−366(3)	−3143(7)	1082(6)	232(4)
C(17)	−914(3)	−3310(5)	1366(5)	196(3)
C(18)	624(3)	−3018(5)	−1105(5)	168(2)
C(19)	422(3)	−3990(6)	−1112(6)	224(3)
O(1)	−417(2)	−2523(2)	392(3)	135(1)
O(2)	716(1)	−2646(2)	−199(3)	140(1)

U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

bond, DIAA typically has large π-conjugated planar structures. Fig. 2 displays the ORTEP structure with the hydrogen bonds and intermolecular π···π stacking interactions. Viewing along the crystallographic *c* axis, the well-conjugated azo molecules show significant intermolecular interactions, including hydrogen bonding and π···π stacking interactions. As shown in Fig. 2, the crystalline ethanol molecules were strongly bonded to the imidazole moiety of the azo molecule by hydrogen bonds. The oxygen atoms of ethanol and the amine or imine N atoms contribute to the formation of hydrogen bonds (N4–H4A–O1, 1.86 Å, 2.684(4) Å, 159.5°; N5–H5A–O2, 2.10 Å, 2.874(4) Å, 150.2°). Interestingly, the azo molecules arrange in a head-to-tail fashion along the *ac* plane due to the strong 'push–pull' electron system. Specifically, the imidazole moiety containing the cyano groups from one molecule interacts with the benzene ring containing the imine group. The shortest intermolecular C···C contact between the imidazole ring and benzene ring is 3.577 Å, belonging to the generally strong π···π interaction. Overall, the conjugated aromatic part of the azo molecule is well co-planar; the dihedral angle between two planes of imidazolyl and anilinyl ring is only 4.0°.

Effects of various pH value and solvent polarity on the absorption spectrum were studied in different solutions. The absorption spectral characteristics of the dye are shown in Figs. 3 and 4.

As shown in Fig. 3, both spectra of the conjugated base and protonated salt of the compound showed significant shift, relative to that of DIAA in methanol. The $\lambda_{\max}$ of the compound in methanol showed large bathochromic effect when 0.1 M HCl was added. It indicated that DIAA existed in cationic form. From the dissociation constants of the conjugate

Table 3
Selected bond length (Å) and bond angles (°)

Bond	Distance	Atom	Angle
N(1)–C(1)	1.359(4)	C(1)–N(1)–C(7)	121.0(3)
N(1)–C(9)	1.470(5)	C(9)–N(1)–C(7)	116.8(3)
N(1)–C(7)	1.470(4)	N(3)–N(2)–C(4)	114.7(3)
N(2)–N(3)	1.257(4)	N(2)–N(3)–C(11)	111.1(3)
N(2)–C(4)	1.410(4)	C(11)–N(4)–C(12)	105.8(3)
N(3)–C(11)	1.409(4)	C(11)–N(5)–C(13)	104.3(3)
N(4)–C(11)	1.360(4)	N(1)–C(1)–C(2)	122.9(3)
N(4)–C(12)	1.382(4)	N(1)–C(1)–C(6)	121.1(3)
N(5)–C(11)	1.311(4)	C(5)–C(4)–N(2)	125.9(3)
N(5)–C(13)	1.367(4)	C(3)–C(4)–N(2)	116.4(3)
N(6)–C(14)	1.130(5)	C(5)–C(6)–C(1)	122.0(3)
N(7)–C(15)	1.138(4)	N(1)–C(7)–C(8)	114.4(3)
C(7)–C(8)	1.496(5)	N(1)–C(9)–C(10)	113.3(4)
C(9)–C(10)	1.480(5)	N(5)–C(11)–N(3)	121.1(3)
C(12)–C(13)	1.358(5)	N(4)–C(11)–N(3)	126.0(3)
C(12)–C(14)	1.416(6)	C(13)–C(12)–N(4)	105.5(3)
C(13)–C(15)	1.446(6)	C(13)–C(12)–C(14)	129.2(3)
C(16)–C(17)	1.333(8)	C(12)–C(13)–N(5)	111.4(3)
C(16)–O(1)	1.377(7)	C(12)–C(13)–C(15)	128.0(3)
C(18)–C(19)	1.424(8)	N(6)–C(14)–C(12)	178.3(5)
C(18)–O(2)	1.493(7)	N(7)–C(15)–C(13)	177.6(5)

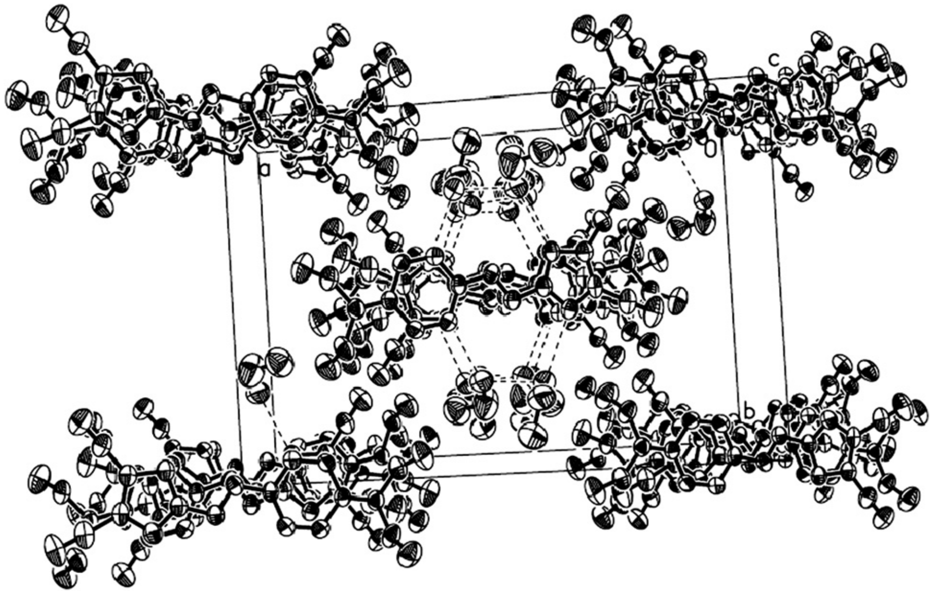

Fig. 2. Crystal packing model along crystallographic *c* axis showing the hydrogen bonds and intermolecular head-to-tail $\pi\cdots\pi$ stacking interactions.

acids of organic bases [15], we know that the nitrogen atoms of the imidazole (N4 or N5, shown in Fig. 1) have the priority of combination with the proton. The formation of protonated salt resulted in an increase in the intramolecular charge transfer ability. Consequently, the energy of the $\pi\cdots\pi^*$ transition was lowered and the bathochromic absorption band of DIAA under acidic condition was observed. On the contrary, when 0.1 M KOH was added the λ_{max} of the compound in methanol showed slightly hypsochromic shift. This may be brought about by the decrease of intramolecular charge transfer ability due to the strong effect between H atom (combined with nitrogen atom of imidazole heterocycle) and O atom of the hydroxyl.

In general, heterocyclic azo disperse dyes tend to show larger solvatochromic effects compared to phenyl azo dyes because of the increase in the polarity, especially in the excited state [16]. Typical absorption spectra of DIAA in different solvents are given in Fig. 4. It showed that the absorption spectra of the dye changed significantly in solvents with different polarity, indicating that this complex was much sensitive to solvent environments. As expected, the $\pi\cdots\pi^*$ transition band of DIAA was strongly solvent-dependent. The visible absorption maximum showed a large hypsochromic shift as the solvent polarity increases, varied from 514 to 464 nm with an increase in the solvent polarity from dichloromethane to methanol.

4. Conclusion

We have reported the synthesis, spectroscopic properties and single-crystal structure of a novel monoazo DIAA. The compound shows significant intermolecular interactions, including hydrogen bonding and $\pi\cdots\pi$ stacking interactions. The azo molecules arrange in a head-to-tail fashion due to

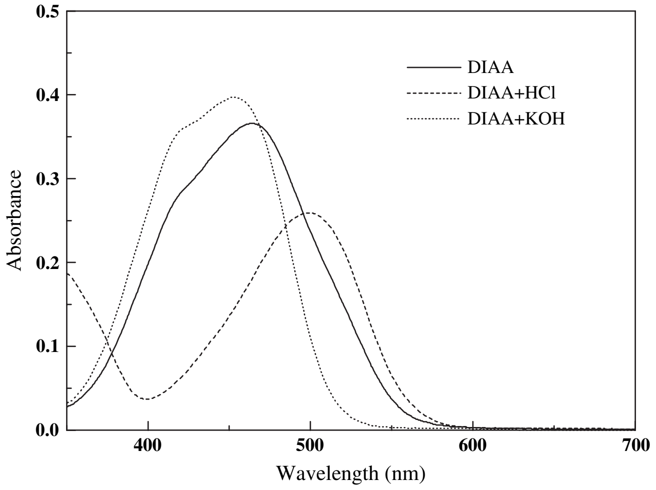

Fig. 3. pH-dependent absorption spectra of DIAA in methanol. $C = 1 \times 10^{-5}$ M.

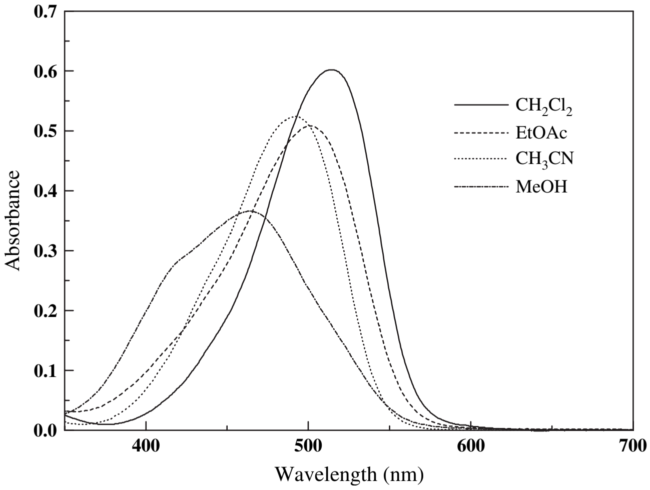

Fig. 4. Solvent-dependent absorption spectra of DIAA. $C = 1 \times 10^{-5}$ M.

strong 'push–pull' electron system. Hence, it is potentially useful to develop new functional third-order nonlinear optical materials. Further work of the spectroscopic and optical properties of DIAA with transition metals is currently under investigation and will be presented in full in due course.

Acknowledgements

This was supported by NSFC (50221201, 50303019, 20333080) and the major state basic research development program (G2000078100) of China.

References

[1] Venkataraman K. The chemistry of synthetic dyes, vol. I. New York: Academic Press; 1952. p. 551–69.
[2] Yen M, Wang I. Synthesis and solvent characteristics of bishetaryl monoazo dyes derived from polysubstituted-2-aminothiophene derivatives. Dyes and Pigments 2005;67(3):183–8.
[3] Sternberg E, Dolphin D. In: Matsuoka M, editor. Infrared absorbing dyes. New York: Plenum; 1990 [chapter 15].
[4] Gordon PF. In: Waring DR, Hallas G, editors. The chemistry and application of dyes. New York: Plenum; 1990 [chapter 8].
[5] Wu SJ, Qian W, Xia ZJ, Zou YG, Wang SQ, Shen SY, et al. Investigation of third-order nonlinearity of an azo dye and its metal-substituted compounds. Chemical Physics Letters 2000;330(5–6):535–40.
[6] Zhang G, Wang S, Gan Q, Zhang Y, Yang G, Ma J, et al. A stable trinuclear zinc cluster assembled from a thiazolylazo dye and zinc acetate: preparation, structural characterization and spectroscopic studies. European Journal of Inorganic Chemistry 2005;20:4186–92.
[7] Sui B, Zhao W, Ma GH, Okamura T, Fan J, Li YZ, et al. Novel Pb(II) coordination frameworks: synthesis, crystal structures and unusual third-order nonlinear optical properties. Journal of Materials Chemistry 2004;14(10):1631–9.
[8] Tian ZY, Huang WT, Xiao DB, Wang SQ, Wu YS, Gong QH, et al. Enhanced and size-tunable third-order nonlinearity of nanoparticles from an azo metal chelate. Chemical Physics Letters 2004;391(4–6):283–7.
[9] Lee GJ, Kim DH, Lee MY. Photophysical properties and photoisomerization processes of embedded in rigid polymer. Applied Optics 1995;34(1):138–43.
[10] Biswas N, Umapathy S. Structures, vibrational frequencies, and normal modes of substituted azo dyes: infrared, Raman, and density functional calculations. Journal of Physical Chemistry A 2000;104(12):2734–45.
[11] Willner I, Rubin S. Control of the structure and functions of biomaterials by light. Angewandte Chemie – International Edition in English 1996;35(4):367–85.
[12] Ertan N, Gürkan P. Synthesis and properties of some azo pyridone dyes and their Cu(II) complexes. Dyes and Pigments 1997;33(2):137–47.
[13] Wang S, Shen S, Xu H. Synthesis, spectroscopic and thermal properties of a series of azo metal chelate dyes. Dyes and Pigments 2000;44(3):195–8.
[14] Wang S, Shen S, Xu H, Gu D, Yin J, Dong X. Metallized thiazolylazo dyes as optical recording materials. Material Science and Engineering B 2001;79(1):45–8.
[15] Perrin DD. Dissociation constants of organic bases in aqueous solution. London: Butterworths; 1965. Suppl. 1972.
[16] Karcı F, Şener İ, Deligöz H. Azocalixarenes. 2: Synthesis, characterization and investigation of the absorption spectra of azocalix[6]arenes containing chromogenic groups. Dyes and Pigments 2004;62(2):131–40.