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STRUCTURAL CHARACTERISATION AND PHOTOLUMINESCENCE OF A PYRIDINE—DIIMINE COMPOUND

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A pyridine—diimine compound *N*,*N*′-[pyridine-2,6-diyldi(*E*)methylylidene]bis(4-chloroaniline) is synthesised by a Schiff base condensation of 2,6-diformylpyridine with 4-chloroaniline in methanol and characterised by spectroscopic and analytical techniques. The molecular structure of the compound is determined by the single crystal X-ray diffraction study. The compound crystallizes in the monoclinic crystal system, *I*2/*c* space group with unit cell parameters $a = 7.0843(12)$ Å, $b = 6.1909(11)$ Å, $c = 36.262(6)$ Å, $\beta = 91.576(3)°$, $V = 1589.8(5)$ Å^3 and $Z = 4$. There is an intermolecular hydrogen bonding in the molecule resulting in a 1D hydrogen bonding chain and these hydrogen bonding chains are linked by Cl…HC(aromatic) interactions forming a 2D network. Crystal packing of the compound is determined by Cl…HC and π—π interactions. In the fluorescence emission spectra in CH_3CN, DMF, DMSO and EtOH, the compound shows only one emission maximum.

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K e y w o r d s: Schiff base, X-ray diffraction, π—π interactions, photoluminescence.

INTRODUCTION

Schiff base condensation reactions yield compounds with wide uses as ligands [1—4]. Schiff bases are reported to possess several biological activities such as antimicrobial [3], antifungal [5], anticancer [6], and cytotoxic [7] activities. There are numerous papers published on transition metal complexes of Schiff bases which regard their antimicrobial activity [8], thermal studies [9], electrochemical properties [10], their use as electrochemical sensors [11] and catalysts for epoxidation of olefins, lactide polymerization, ring opening of epoxides, and Michael reactions [12—14]. Transition metal complexes derived from Schiff bases have been playing a central role in the development of coordination chemistry. The azomethine/imine group (—C=N—) of Schiff bases forms stable complexes with transition metals through the coordination of nitrogen atoms. Schiff base ligands are capable of coordinating to many different metals and can stabilize them in various oxidation states, thus enabling the use of Schiff base metal complexes in a large variety of catalytic reactions [12—14].

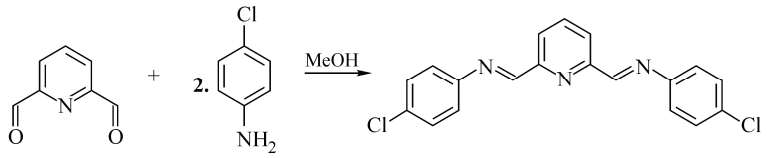
In this study, a Schiff base ligand *N*,*N*′-[pyridine-2,6-diyldi(*E*)methylylidene]bis(4-chloroaniline) was prepared and characterised by analytic and spectroscopic methods. The compound was structurally characterized by the single crystal X-ray diffraction technique. Additionally, the electronic and luminescence properties of the compound were investigated.

EXPERIMENTAL

All starting materials were obtained from Aldrich and Fluka, and used without further purification. The ^{13}C and ^{1}H NMR spectral measurements were performed on Bruker Avance 400 (400 MHz). Mass spectra were recorded on a Thermo Fisher Exactive + Triversa Nanomate mass spectrometer. The IR spectrum was recorded on a Perkin Elmer Paragon 1000 PC using a KBr pellet. CHN analysis was performed using a CE-440 Elemental analyzer. The electronic spectra in the 200—900 nm range were obtained on a Shimadzu UV-1800 UV-Vis spectrophotometer. The single photon fluorescence spectra of the compound were measured on a PerkinElmer LS55 luminescence spectrometer.

Data collection for X-ray crystallography was completed using a Bruker APEX2 CCD diffractometer and data reduction was performed using Bruker SAINT. SHELXTL was used to solve and refine the structure [15].

Preparation of the compound. The titled compound was prepared by the reaction of one equivalent of 2,6-diformylpyridine and two equivalents of 4-chloroaniline in MeOH. A solution of 4-chloroaniline (0.255 g, 2 mmol) in MeOH (20 ml) was added to a MeOH (20 ml) solution of 2,6-diformylpyridine (0.135 g, 1 mmol) and the resulting solution was stirred for 4 h at room temperature. The cream color precipitate was filtered and washed with cold MeOH (10 ml) and diethylether (10 ml) and dried in air. Yield: 0.319 g (90 %), colour: cream. M.p.: 192—195 °C. Analysis Calc. for $C_{22}H_{21}N_3O_2$ (%): C 64.42, H 3.70, N 11.86. Found (%): C 64.27, H 3.62, N 11.47. IR (cm^{-1}) selected bands: 2998, 1625, 1579, 1565, 1481, 1335, 1199, 1089, 1009, 946, 836, 813, 739, 724, 674, 517.



X-ray crystallography. A single crystal of dimensions 0.56×0.25×0.11 mm was chosen for the diffraction experiment. Data were collected at 150(2) K on a Bruker ApexII CCD diffractometer using MoK_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F^2 using all the reflections [16]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon atoms were inserted at the calculated positions using a riding model. Details of the crystal data and refinement: $C_{19}H_{13}N_3Cl_2$, M = 354.22, monoclinic, space group $I2/c$, a = 7.0843(12), b = 6.1909(11), c = 36.262(6) Å; β = 91.576(3)°, V = 1589.8(5) Å^3, Z = 4, μ = 0.0413 mm^{-1}, colorless crystal, 8742 reflections collected, 99.2 % completeness to θ = 31.57°, 2481 independent (R_{int} = 0.0202), R_1 = 0.0326, wR_2 = 0.0890 ($I > 2\sigma(I)$), R_1 = 0.0366, wR_2 = 0.0919 (all data), CCDC 997206. Bond lengths and angles are given in Table 1. Hydrogen bond parameters are given in Table 1.

RESULTS AND DISCUSSION

2,6-Diformypyridine was prepared by the oxidation of 2,6-pyridinedimethanol according to the reported method [17]. The titled compound was prepared according to the reported method [18] by reacting one equivalent of 2,6-diformypyridine with two equivalents of 4-chloro aniline in methanol. The cream coloured product is stable at room temperature in the solid state without decomposition. The compound is partially soluble in methanol and ethanol, acetonitrile, chloroform, dichloromethane, DMF, and DMSO and not soluble in water.

The molecule has two azomethine groups and two 4-chloroaniline units on each side of pyridine. Elemental analysis results are given in the EXPERIMENTAL section and are in good agreement with the calculated values. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, and the spectral data are given in the EXPERIMENTAL section. ^{1}H and ^{13}C NMR spectra are displayed in Figs. 1 and 2 respectively. The compound shows mirror symmetry in the solution. In the ^{1}H NMR spectrum, a singlet at δ 8.66 ppm was assigned to azomethyne protons (—N=CH—). Aromatic ring protons were observed in the range of δ 7.27—8.30 ppm. A doublet at δ 8.30 ppm and a triplet at δ 7.99 ppm in the 2:1

Table 1

Bond lengths (Å) *and angles* (deg.) *for the compound*

Cl(1)—C(3)	1.7402(11)	C(3)—C(4)	1.3905(16)	C(7)—N(1)—C(6)	117.75(10)	C(1)—C(6)—C(5)	119.42(10)
N(1)—C(7)	1.2734(14)	C(4)—C(5)	1.3899(15)	C(2)—C(1)—C(6)	120.62(10)	C(1)—C(6)—N(1)	122.72(9)
N(1)—C(6)	1.4197(14)	C(5)—C(6)	1.3997(15)	C(8)$^{\#}$—N(2)—C(8)	117.79(13)	C(5)—C(6)—N(1)	117.85(10)
C(1)—C(2)	1.3879(15)	C(7)—C(8)	1.4734(15)	C(1)—C(2)—C(3)	118.97(10)	N(1)—C(7)—C(8)	122.47(10)
C(1)—C(6)	1.3981(15)	C(8)—C(9)	1.3943(15)	C(4)—C(3)—C(2)	121.42(10)	N(2)—C(8)—C(9)	122.93(10)
N(2)—C(8)$^{\#}$	1.3449(12)	C(9)—C(10)	1.3887(14)	C(4)—C(3)—Cl(1)	119.52(8)	N(2)—C(8)—C(7)	114.85(9)
N(2)—C(8)	1.3449(12)	C(10)—C(9)$^{\#}$	1.3887(14)	C(2)—C(3)—Cl(1)	119.05(9)	C(9)—C(8)—C(7)	122.21(10)
C(2)—C(3)	1.3913(15)			C(5)—C(4)—C(3)	119.15(10)	C(10)—C(9)—C(8)	118.69(11)
				C(4)—C(5)—C(6)	120.32(10)	C(9)$^{\#}$—C(10)—C(9)	118.94(15

Symmetry transformations used to generate equivalent atoms: # $-x, y, -z+1/2$.

ratio were assigned to the pyridine protons. Two doublets at δ 7.29 ppm and 7.40 ppm in the 1:1 ratio were assigned to the benzene ring protons. In the ^{13}C NMR spectrum of the compound, the signal at δ 160.36 ppm could be assigned to azomethine carbon atoms (—N=C—). All the other aromatic carbon atom shifts were observed in the range of δ 122.52—154.44 ppm. The NMR spectra of the compound indicate that there is no organic impurity in the sample.

The ESI mass spectrum of the titled compound showed signals at *m*/*z* 355 (40 %) and 377 (100 %) assigned to singly charged molecular $[M+H]^+$ and $[M+Na]^+$ ions respectively. The infrared spectrum data of the compound are given in the EXPERIMENTAL section. The azomethine $\nu_{(CH=N)}$ vibration was observed at 1625 cm^{-1}.

Structure of the compound. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a chloroform solution of the compound. The molecular structure of the com pound is shown in Fig. 3. The compound crystallizes in the monoclinic crystal system, *I*2/*c* space group with unit cell parameters $a = 7.0843(12)$ Å, $b = 6.1909(11)$ Å, $c = 36.262(6)$ Å, $\beta = 91.576(3)°$, $V = 1589.8(5)$ Å^3 and $Z = 4$. All bond lengths and angles are within the normal ranges. All bond

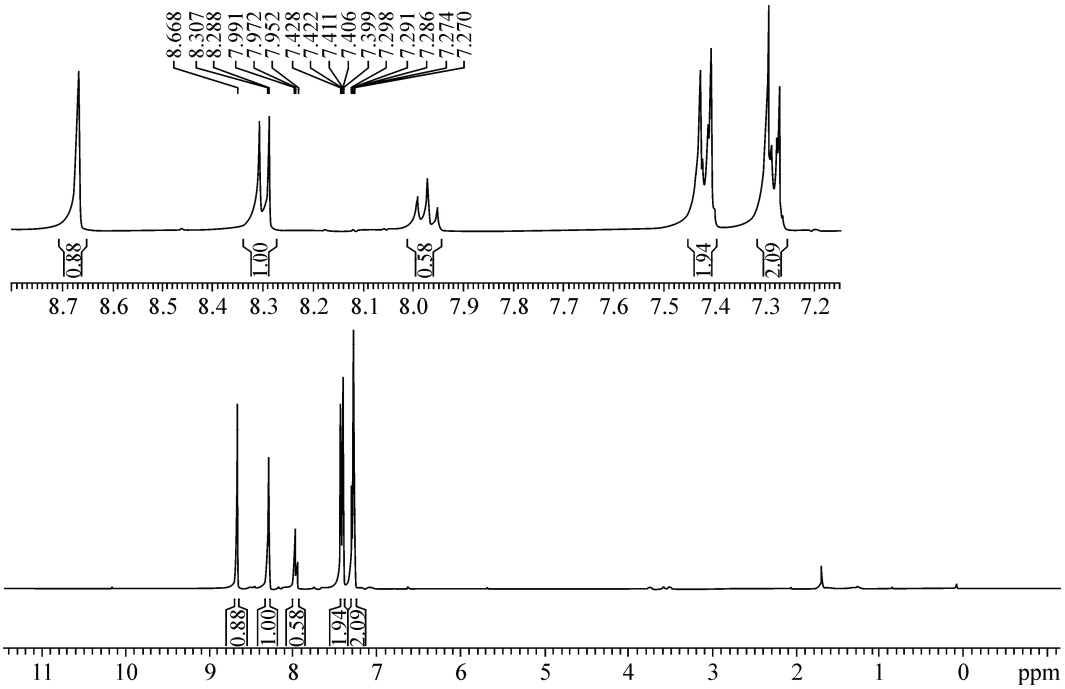


Fig. 1. ^{1}H NMR spectrum of the compound

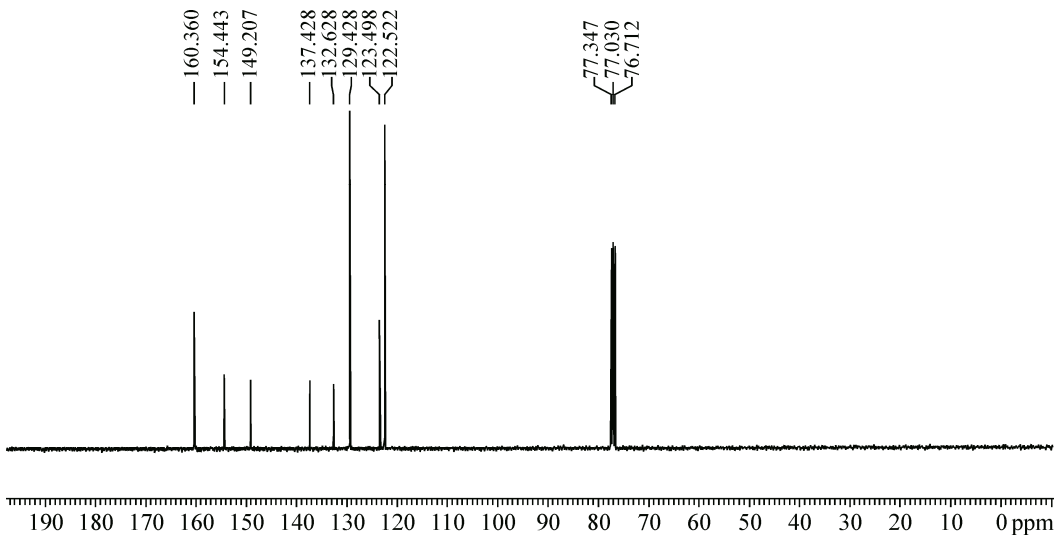


Fig. 2. ^{13}C NMR spectrum of the compound

lengths and angles in the pyridine and phenyl rings have normal C(sp^2)—C(sp^2) values and are in the expected ranges (Table 1). The N2 and C10 atoms of the pyridine ring are situated on a two-fold axis and the asymmetric unit contains half of the compound. The N1—C7 bond length of 1.2734(14) indicates a double bond (C=N) character, which is in good agreement with the published values. Outer phenyl rings (C1/C6 and C1A/C6A) adopt the *trans* configuration with regard to the azo-methine double bond (—N1=C7—).

There is an intermolecular hydrogen bonding (C10—H···N1) in the molecule resulting in a 1D hydrogen bonding chain (Table 2, Fig. 4). Hydrogen bonding chains are linked by Cl…HC(aromatic) interactions forming a 2D network shown in Fig. 4.

In the structure, the outer phenyl rings are twisted with respect to the central pyridine ring. The mean C1/C6 plane is at 30.40(3)° to the pyridine (N2/C8A) ring. This is possibly a consequence of the intermolecular interactions in the lattice. The N1—C7 section of the molecules is stacked with the C7—C8 section of an adjacent molecule under the symmetry operation of x–1/2, 1/2–y, z (Fig. 5); N1 and C7***** are separated by a distance of 3.334 Å. Crystal packing of the compound is determined by Cl…HC and π—π interactions. The packing plot of the compound is shown in Fig. 6.

T a b l e 2

Hydrogen bonds for the compound (Å *and* deg.)

D—H…A	*d*(D—H)	*d*(H…A)	*d*(D…A)	∠(DHA)
C(10)—H(10)…N(2)$^{\#}$	0.93	2.47	3.397(2)	180.0

Symmetry transformations used to generate equivalent atoms: # x, y+1, z.

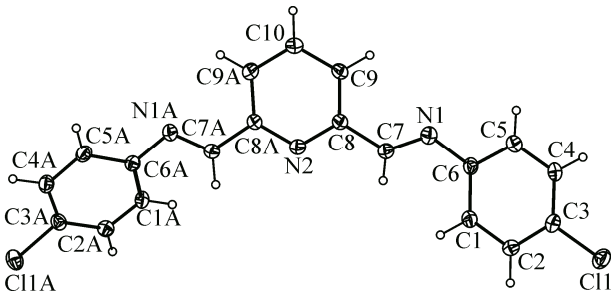


Fig. 3. Perspective view of the titled compound with atom numbering and thermal ellipsoids at a 50 % probability level

It is informative to compare the crystal structures of the compound with fluoro, methyl, and metoxy analogues prepared by Wong et al. [18]. The crystal structures of fluoro, methyl, and metoxy analogues resemble each other. Both published structures and the compound reported here show the same intermolecular hydrogen bonding (CH(pyridine)|N(pyridine)). The structure of the fluoro compound shows π—π interactions similarly to the chloro compound reported here [18].

Photoluminescence properties of the compound. The absorption spectra of the compound were studied in ethanol, acetonitrile, DMSO, and DMF (10^{-5} M). Photo-

physical properties are summarized in Table 3. The absorption spectra of the compound show two absorption maxima. The absorptions in the 250—290 nm range can be assigned to π—π* transitions due to the presence of π electrons (aromatic rings and imine groups) in the compound. The bands in the

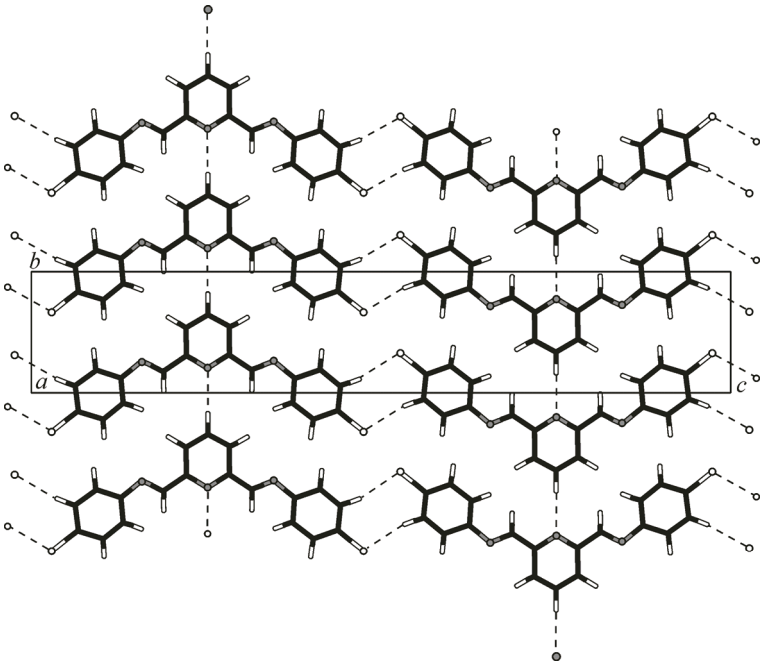


Fig. 4. CH···N and CH···Cl interactions within the structure

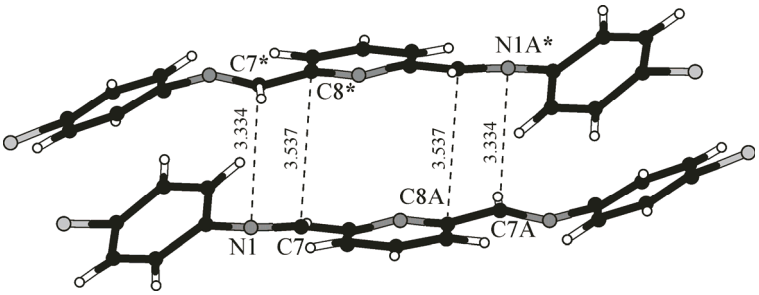


Fig. 5. π—π Interactions within the structure.
Symmetry codes: * 1/2+*x*, 1/2–*y*, *z*, A: –*x*, *y*, –*z*+1/2

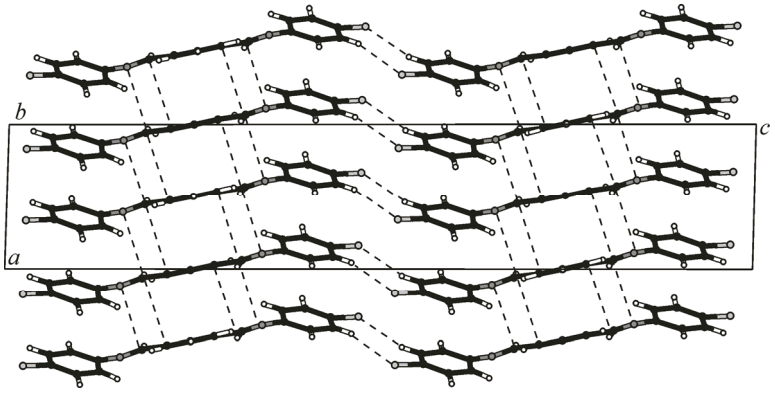


Fig. 6. Packing plot of the compound showing CH···Cl interactions within the structure

300—350 nm range can be attributed to the *n*—π* transitions. The *n*—π* transitions are shifted to longer wavenumbers in ethanol, CH_3CN, DMF, and DMSO solvents.

T a b l e 3

UV-vis *absorption*, *emission*, *and excitation spectral data of the compound*

Solvent	Ems.	Exc.	Abs.(ε)
Acetonitrile	385	255	265 (2.65×10^{-4}) 326 (3.26×10^{-4})
Ethanol	390	250	264 (2.64×10^{-4}) 327 (3.27×10^{-4})
Dimethylformamide	386	249	264 (2.22×10^{-4}) 340 (3.40×10^{-4})
Dimethylsulfoxide	388	245	262 (2.62×10^{-4}) 309 (3.09×10^{-4})

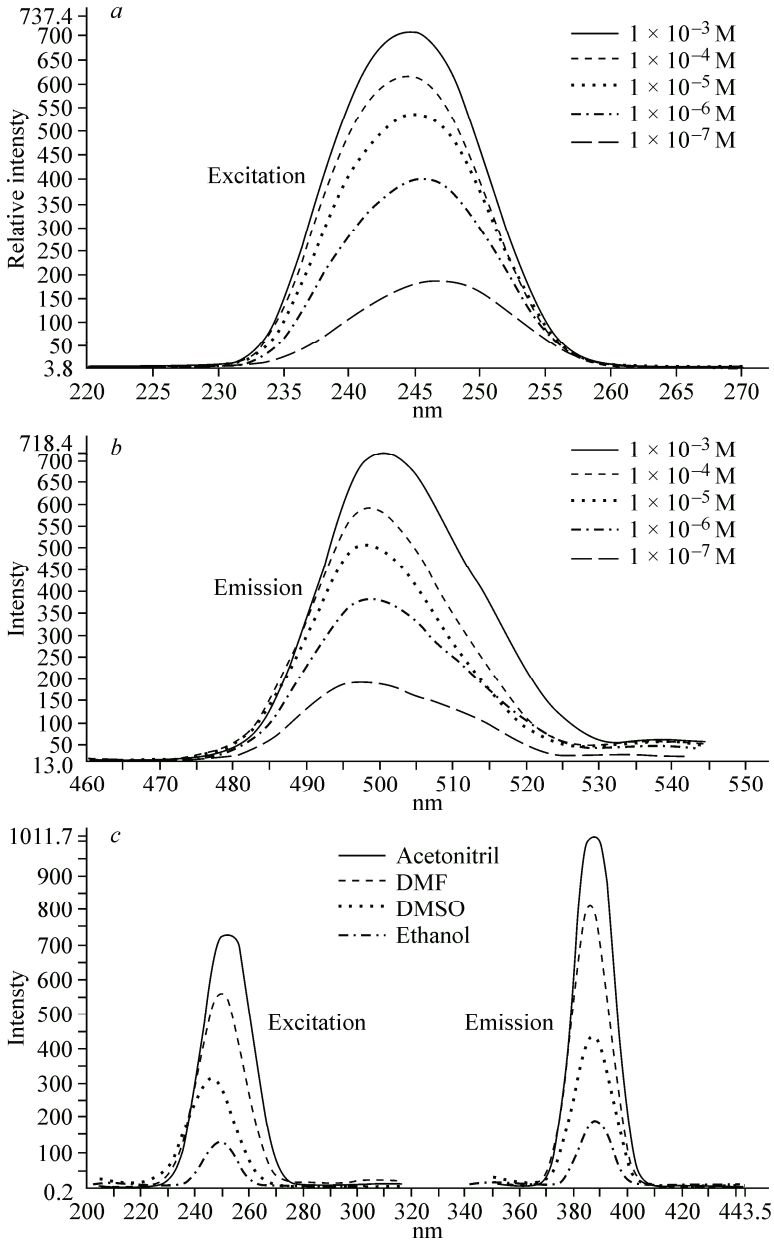


Fig. 7. Fluorescence emission and excitation spectra of the compound

The emission and excitation spectra of the Schiff base in various solvents at different concentrations (10^{-5} M) are shown in Fig. 7, *c*. In the fluorescence emission spectra in CH_3CN, DMF, DMSO, and EtOH solutions, the compound gives only one emission maximum band in the range of 360—410 nm in all solvents used. The highest and lowest emission intensities were observed in CH_3CN and EtOH, respectively. As the polarity of the solvent increases, the emission bands shift to higher wavelength values. The effect of different concentrations on the photoluminecence properties of the diimine compound was investigated in the 1.0×10^{-3}—1.0×10^{-7} M range in DMF. At room temperature, the compound exhibits similar emission spectra in the UV-vis region (Fig. 7, *a*, *b*). At the 1.0×10^{-3} M concentration, the compound shows the highest emission peak in the 475—525 nm range. As the compound concentration increases, both emission and excitation intensities increase [19—20]. The emission peak of the compound are shifted to higher wavelenght values when the concentration of the compound increases.

CONCLUSIONS

In summary, the Schiff base compound *N*,*N*′-[pyridine-2,6-diyldi(*E*)methylylidene]bis(4-chloroaniline) was prepared *via* a Schiff base condensation reaction and characterized by spectroscopic and analytical techniques. The molecular structure of the compound was successfully determined by single crystal X-ray diffraction. The intermolecular hydrogen bonding was observed in the structure, which forms a 1D hydrogen bonding chain. Crystal packing of the compound is determined by Cl…HC and π—π interactions. In the fluorescence emission spectrum in the CH_3CN, DMF, DMSO and EtOH solutions the Schiff base shows only one emission maximum.

CCDC 997206 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre 12 Union Road Cambridge CB2 1EZ, UK Fax: +44(0)1223-336033.

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