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New Benzo-15-Crown-5 Ethers Featuring Salicylic Schiff Base Substitutions – Synthesis, Complexes and Structural Study *

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Abstract

Condensation reactions between 4′-formyl-5′-hydroxybenzo-15-crown-5 and 2-aminopyridine, 2-amino-6-methylpyridine, 2-amino-4-methylpyridine or 2-(aminomethyl)furan yielded the new laterally functionalized crown ethers **1–4**. The crown compounds **1–3** form crystalline 1:1 (Na^+:ligand) complexes **1a–3a** with sodium perchlorate. Ligands and complexes have been characterized by elemental analyses, IR, UV-Vis, ^{1}H-, ^{13}C-NMR and mass spectra. The tautomeric equilibria (phenol-imine, O–H···N and keto-amine, O···H–N forms) have been systematically studied by using UV-Vis absorption spectra. The spectra of the ligands **1–4** and complexes **1a–3a** were recorded in polar, non-polar, acidic, and basic media. In solutions of polar solvents, tautomeric interconversion of the Schiff base into the keto-amine form has been observed. A crystal structure [monoclinic, space group $P2_1/c$, $a = 14.292(2)$, $b = 9.449(6)$, $c = 16.059(2)$ Å, $\beta = 114.20(1)°$, $V = 1978.4(13)$ Å^3, $Z = 4$ and $D_x = 1.314$ g cm^{-3}] shows that compound **4** is in the form of phenol-imine in solid state. There is a strong intramolecular [O–H···N 1.78(6), O···N 2.581(7), O–H 0.89(6) Å and N···H–O 148.4(5)°] hydrogen bond between the phenolic oxygen and imine nitrogen atoms. The C=N imine bond reveals a trans planar (1E) configuration. The molecules stack in columns parallel to the a/c plane of the unit cell.

Introduction

Crown compounds with additional donor atom(s) in the side arm(s) have been synthesized in order to alter the cation binding ability and selectivity of the parent crown ethers [1, 2]. On that score, benzo condensed crown compounds having reactive formyl or hydroxy substituents at the aromatic ring are considered to be interesting starting materials [3–6]. Crown ether Schiff base ligands have been synthesized in this way and extensively studied with respect to their affinity to interact with alkali and transition metal ions [3–7]. Schiff bases formed by condensation of aromatic amines with aromatic aldehydes that contain an ortho hydroxy group can exist in two tautomers, namely phenol-imine and keto-amine forms [4–6, 8–10]. The proton transfer plays an important role in the thermo- and photo-chromism of Schiff bases, as well as in their biological properties [10]. Consequently, it is evident that a closely related phenomenon of interest is the possibility of tautomeric isomerism in ortho-hydroxy Schiff base type crown compounds and their complexes. The metal complexes may facilitate proton transfer from the phenolic oxygen to the imine nitrogen atom and serve as models of relevance to bioinorganic chemistry such as metalloproteins and metalloenzymes [11]. Moreover, the precise mode of molecular recognition between macrocyclic host compounds and their guests provides a good opportunity for studying key aspects of supramolecular chemistry, which are also significant in a variety of disciplines including chemistry, biology, physics, medicine and related science and technology [12].

In this paper, we describe the synthesis of four new benzo-15-crown-5 ether ligands **1–4** featuring different ortho-hydroxy Schiff base type laterally functions, including sodium perchlorate complexes **1a–3a** (Scheme 1). We also report examination of the range of keto-amine and phenol-imine forms of the ligands **1–4** by using UV-Vis spectral data in solution, IR and X-ray crystallographic techniques in the solid state.

Experimental

Physical measurements

Melting points were determined with a Gallencamp apparatus and are uncorrected. Elemental analyses were performed on a LECO CHNS-932C instrument. IR spectra were recorded with a Mattson 1000 FTIR spectrometer using KBr

* Supplementary data relating to this article are deposited with the British Library as Supplementary Publication No. 82302.

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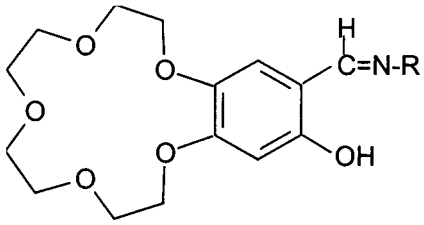
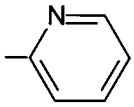
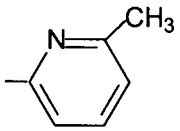
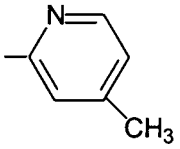
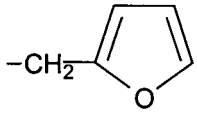
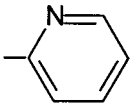
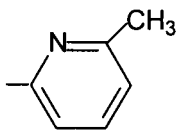
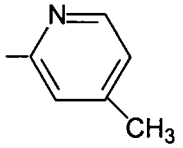
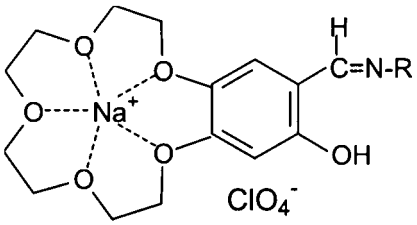


Compounds	R
1	
2	
3	
4	

Complexes	R
1a	
2a	
3a	



Scheme 1. Crown compounds and complexes.

Table 1. Analytical and experimental details

Comp.	Formula	M.p. (°C)	Yield (%)	Elemental analyses (%) calcd. (found)			M(M^+) calcd. (found)
				C	H	N	
1[a]	$C_{20}H_{24}O_6N_2$	138	75	61.83(61.36)	6.23(6.18)	7.22(7.26)	388(388)
2[a]	$C_{21}H_{26}O_6N_2$	130	78	62.67(62.84)	6.51(6.51)	6.96(7.28)	402(403)
3[a]	$C_{21}H_{26}O_6N_2$	125	65	62.67(62.34)	6.51(6.67)	6.96(6.58)	402(402)
4	$C_{20}H_{25}O_7N$	93	69	61.36(61.37)	6.44(6.28)	3.58(3.57)	391(391)
1a	$C_{20}H_{24}O_6N_2NaClO_4$	219	59	47.02(46.83)	4.74(4.61)	5.4(5.37)	–
2a[a]	$C_{21}H_{26}O_6N_2NaClO_4$	269	71	48.05(47.76)	4.99(4.59)	5.34(4.99)	524(402)
3a	$C_{21}H_{26}O_6N_2NaClO_4$	190	48	48.05(47.70)	4.99(4.73)	5.34(5.01)	–

[a]Based on the mass of the most abundant isotope.

Table 2. Crystallographic data for **4**

Formula	$C_{20}H_{25}NO_7$
Formula weight	391.41
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell constants	
a/Å	14.292(2)
b/Å	9.449(6)
c/Å	16.059(2)
β/°	114.20(1)
V/Å^3	1978.4(13)
Z	4
D_{calc}/Mg m^{-3}	1.314
μ_{calc}/mm^{-1}	0.100
Crystal dimensions/mm	0.15 × 0.15 × 0.30
Reflections measured	2678
2θ(max)/°	52.6
Range of h, k, l	$-14 < h < 15, 0 < k < 10, -17 < l < 0$
Number of reflections with $I > 2\sigma(I)$	1332
Number of reflections used in refinement	2678
No. of parameters var.	257
Weighting scheme	$w = 1/[\sigma^2(Fo^2) + (0.1376P)^2 + 0.2538P]$ where $P = (Fo^2 + 2Fc^2)/3$
Goodness of fit	1.022
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.0649
$R_w = [\Sigma(w\|F_o\| - \|F_c\|)^2/w\|F_o\|^2]^{1/2}$	0.1950
	0.267/−0.216

Table 3. Selected IR bands

Comp.	$\nu_{C-H_{(aliph.)}}$	$\nu_{C=N}$	$\nu_{C-O-C_{(arom.)}}$	$\nu_{C-O-C_{(aliph.)}}$	$\nu_{ClO_4^-}$
1	2924, 2861	1623	1274	1130–1073	–
2	2924, 2867	1624	1272	1138–1049	–
3	2931, 2860	1611	1272	1142–1047	–
4	2917, 2868	1630	1270	1134–1057	–
1a	2922, 2874	1629	1279	1211–1053	1091, 626
2a	2918, 2877	1626	1278	1120–1030	1093, 626
3a	2922, 2853	1632	1279	1120–1030	1098, 626

pellets. ^{1}H and ^{13}C-NMR (400 MHz) spectra were recorded with a Bruker DPX FT-NMR spectrometer in $CDCl_3$, unless stated otherwise, using residuals $CHCl_3$ (δ = 7.26) and $CDCl_3$ (δ = 77.00) as the internal standards, respectively. UV-Vis spectra were obtained using a UNICAM UV2-100 series spectrometer. Mass spectra were obtained on a VG-ZAPSPEC spectrometer according to electron impact (EI, 70 eV).

Materials

Tetraethylene glycol dichloride [13], benzo-15-crown-5 [14], 4′-formylbenzo-15-crown-5 [15], 4′-hydroxybenzo-15-crown-5 [16, 17] and 4′-formyl-5′-hydroxy-benzo-15-crown-5 [3] were synthesized according to literature methods. Tetrahydrofuran (THF), diethylether and dichloromethane were dried by refluxing over sodium and phosphorus pentaoxide, respectively. The amines were purchased from Merck Chemical Co. Unless otherwise stated, commercial grade chemicals were used without further purification.

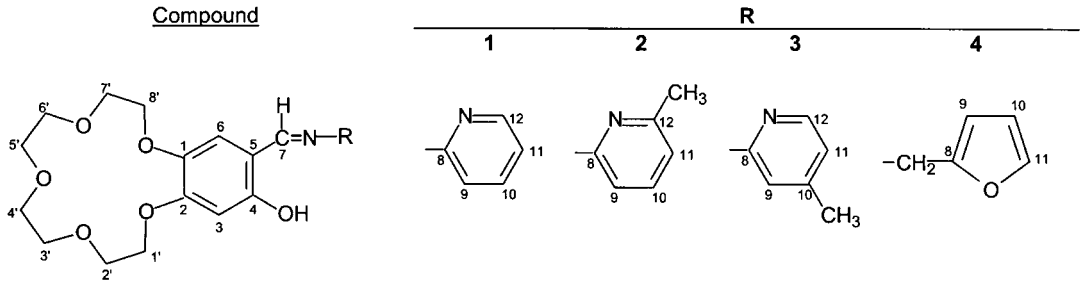
Preparations

*General procedure for the synthesis of **1–4***

To a solution of 4′-formyl-5′-hydroxybenzo-15-crown-5, (1.00 g, 3.20 mmol) in dry methanol (50 mL) was added dropwise a solution of 2-aminopyridine, 2-amino-6-methylpyridine or 2-amino-4-methylpyridine (3.20 mmol) in dry methanol (50 mL). In the case of compound **4**, the crown aldehyde and furfurylamine were dissolved in dry THF. The reaction mixture was heated to reflux and stirred for 1 h. The solvent was evaporated and the crude product recrystallized from n-heptane to yield yellow crystals of

Table 4. ^{1}H-NMR spectral data of the crown ethers (in $CDCl_3$; δ in ppm; s: singlet, d: doublet, t: triplet; m: multiplet, bs: broad singlet)

Comp.	$-CH_3$	$-CH_2$	$O-CH_2-CH_2-O$	Ar–H_3	Ar–H_6	Ar–H_9	Ar–H_{10}	Ar–H_{11}	Ar–H_{12}	H–C=N	OH
1	-	-	3.70–4.20 (m, 16H)	6.90 (s, 1H)	6.45 (s, 1H)	7.24 (d, 1H) ^3J = 7.8 Hz ^4J = 1.8 Hz ^4J = 1.6 Hz	7.75 (m, 1H) ^3J = 7.8 Hz ^3J = 6.9 Hz ^3J = 1.8 Hz	7.16 (m, 1H) ^3J = 6.9 Hz ^3J = 6.1 Hz	8.48 (m, 1H) ^3J = 6.1 Hz ^4J = 1.6 Hz	9.23 (s, 1H)	13.90 (bs.1H)
2	2.57 (s, 3H)	–	4.10–4.19 (m, 16H)	6.89 (s, 1H)	6.43 (s, 1H)	7.02 (d, 1H) ^3J = 7.7 Hz	7.61 (t, 1H) ^3J = 7.7 Hz	7.02 (d, 1H) ^3J = 7.7 Hz	–	9.21 (s, 1H)	14.10 (bs, 1H)
3	2.39 (s, 3H)	–	3.64–4.34 (m, 16H)	6.83 (s, 1H)	6.42 (s, 1H)	7.04 (s, 1H)	–	6.98 (d, 1H) ^3J = 5.1 Hz	8.31 (d, 1H) ^3J = 5.1 Hz	9.16 (s, 1H)	6.70 (s, 1H)
4	–	4.71(s, 2H)	3.73–4.15 (m, 16H)	6.75 (s, 1H)	6.44 (s, 1H)	6.28 (m, 1H)	6.36 (m, 1H)	7.40 (m, 1H)	–	8.19 (s, 1H)	13.37 (bs, 1H)
1a	–	–	3.78–4.30 (m, 16H)	7.08 (s, 1H)	6.96 (s, 1H)	7.29 (d, 1H) ^3J = 7.4 Hz ^4J = 1.9 Hz	7.80 (m, 1H) ^3J = 7.4 Hz ^3J = 6.3 Hz ^4J = 1.4 Hz	7.22 (m, 1H) ^3J = 6.3 Hz ^3J = 6.0 Hz ^4J = 1.9 Hz	8.51 (m, 1H) ^3J = 6.0 Hz ^4J = 1.4 Hz	9.26 (s, 1H)	13.97 (bs, 1H)
2a	2.47 (s, 3H)	–	3.65–4.18 (m, 16H)	7.02 (s, 1H)	6.46 (s, 1H)	7.00 (d, 1H) ^3J = 7.7 Hz	7.59 (m, 1H) ^3J = 7.7 Hz	6.97 (d, 1H) ^3J = 7.7 Hz	–	9.21 (s, 1H)	13.90 (s, 1H)
3a	2.33 (s, 3H)	–	3.67–4.19 (m, 16H)	6.81 (s, 1H)	6.41 (s, 1H)	7.19 (s, 1H)	–	6.95 (d, 1H) ^3J =5.3 Hz	8.25 (d, 1H) ^3J = 5.3 Hz	9.16 (s, 1H)	13.93 (s, 1H)



Numbering of the crown ether carbons and protons for NMR spectra.

Table 5. Selected ^{13}C-NMR spectral data (δ in ppm)[a]

Comp.	C_1–C_3, C_5, C_6, C_9–C_{12}	$C_{1'}$–$C_{8'}$	C_4	C_7	CH_3	C_8
1	156.66;149.26; 142.41; 138.75; 122.00; 119.41; 118.08; 111.37; 102.17	71.53; 71.38; 71.07; 70.88; 70.64; 70.10; 69.45; 68.72	161.51	163.00	–	158.29
2	156.70; 156.60; 142.38; 138.84; 121.48; 117.26; 115.98; 111.97; 102.27	71.57; 71.41; 71.10; 70.87; 70.67; 70.13; 69.48; 68.68	162.00	164.90	24.75	159.37
3	150.14; 148.84; 142.34; 123.12; 119.79; 117.74; 116.70; 109.47; 102.28	71.53; 71.38; 71.07; 70.93; 70.78; 70.65; 70.10; 68.69	160.89	164.17	21.34	156.87
4	151.70; 142.86; 141.69; 117.63; 110.83 110.00; 108.24; 102.04	71.32; 71.13; 71.06; 70.99; 70.54; 70.13; 69.47; 68.45	160.09	165.27	54.53[b]	154.63
1a	157.04; 149.34; 140.48; 138.94; 122.50; 119.65; 115.60; 111.92; 102.50	69.88; 69.59; 68.63; 68.44; 68.34; 68.07; 67.88; 67.75	161.96	162.37	–	159.78
2a	160.92; 159.12; 145.38; 143.87; 126.85; 122.87; 120.92; 116.58; 107.20	74.40; 74.36; 74.02 73.76; 73.57; 73.52 72.98; 72.29	166.25	167.62	29.50	163.15
3a	149.03; 148.93; 142.18; 122.56; 118.65; 117.68; 113.12; 105.73; 102.09	70.96; 69.82; 68.96 68.13; 68.03; 67.99 67.61; 67.09	160.96	162.26	21.06	155.93

[a]For the numbering scheme, see Table 4.
[b]–CH_2– carbon.

compounds **1–4**. Details of the individual compounds are given in Table 1.

*General procedure for the preparation of the sodium complexes **1a–3a***

The ligands **1–3** (1.00 mmol) suspended in dry methanol (20 mL) were added to a solution of $NaClO_4$ (0.12 g, 1.00 mmol) in methanol. The mixture was stirred and heated to reflux for 1 h. The yellow product was filtered off and washed with diethylether. Details of the individual compounds are summerized in Table 1.

The sodium complex of compound **4** could not be isolated as pure.

Crystallography

The crystals suitable for X-ray analysis were obtained by crystallization of **4** from n-heptane. The diffraction study was performed with an Enraf-Nomius CAD-4 diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 298 K. Experimental data, methods and the procedures to elucidate the structure and other related parameters are given in Table 2. Intensity data were collected in the ω-2θ scan mode. The structure was solved by direct methods (SHELXS-97 [18]). The atom H(18) was located in a difference map and refined isotropically. The positions of the remaining H atoms were calculated geometrically at distances of 0.93 (CH) and 0.97 Å (CH_2) from the corresponding C atoms [19], and a riding model was used during the refinement process (SHELXL-97 [18]). Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre CCDC 187510. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)3 36-0 33; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposite@ccdc.cam.ac.uk).

Results and discussion

Syntheses

The details respecting the syntheses of **1–4** and **1a–3a** are given above (see pp. 3). The structures of the crown compounds and complexes have been confirmed by elemental analyses, IR, ^{1}H-,^{13}C-NMR, UV-Vis and MS. All of these new compounds gave spectroscopic and analytical data in accordance with the proposed structure (Tables 1 and 3–5).

Spectroscopy

IR spectra. In the IR spectra of the ligands (**1–4**) and complexes (**1a–3a**) no band is observed in the region 3650–3590 cm^{-1} attributable to the stretching vibration of the free phenolic hydroxy group [20], indicating the formation of a cyclic intramolecular hydrogen bond. This structural behaviour, i.e. the existence of an intramolecular hydrogen bond between the hydroxyl oxygen and the nitrogen atom is further corroborated by the below X-ray structural result. For the uncomplexed ligands **1–4** relatively strong bands attributable to $\nu_{C=N}$ are detected at 1611–1630 cm^{-1}. In the sodium complexes **1a–3a** these bands are a little shifted to higher frequencies. The aromatic and aliphatic (C–O–C) ether stretching bands of the ligands and complexes are

Table 6. UV-Vis spectral data and values of tautomeric constants in various solvents

Comp.	Solvent	λ, nm (log ϵ)	% Keto isomer[a]		
			Solvent medium	Acidic medium[b]	Basic medium[c]
1	DMSO	378(3.28), 442(2.64)	18.9	50.1	22.3
	EtOH	372(3.26), 440(2.92)	31.6	0.0	31.1
	$CHCl_3$	376(3.22), 448(2.63)	20.8	40.9	23.3
	C_6H_{12}	378(3.30)	0.0	46.9	0.0
2	DMSO	380(3.37), 438(2.89)	24.8	54.2	28.6
	EtOH	372(3.28), 448(3.06)	37.4	0.0	20.8
	$CHCl_3$	374(3.30), 450(2.82)	24.9	44.0	26.7
	C_6H_{12}	378(3.41)	0.0	47.2	0.0
3	DMSO	376(3.37), 436(2.91)	25.8	53.3	28.5
	EtOH	372(3.28), 446(2.99)	33.9	0.0	33.9
	$CHCl_3$	374(3.27), 448(2.73)	22.4	38.9	24.9
	C_6H_{12}	378(3.40)	0.0	44.2	0.0
4	DMSO	332(4.29), 410(3.52)	14.5	0.0	0.0
	EtOH	302(4.16), 408(3.85)	32.4	0.0	27.6
	$CHCl_3$	330(4.31), 412(3.41)	10.0	0.0	10.0
	C_6H_{12}	332(4.06)	0.0	0.0	0.0
1a[d]	DMSO	352(3.96), 448(3.00)	9.9	33.6	8.9
	EtOH	348(3.97), 438(3.43)	22.3	0.0	23.5
	$CHCl_3$	354(3.93), 446(3.08)	12.4	0.0	13.2
	C_6H_{12}	–	–	–	–
2a[d]	DMSO	380(3.98), 458(3.17)	13.4	55.2	14.5
	EtOH	350(3.92), 450(3.40)	33.2	0.0	23.5
	$CHCl_3$	370(3.96), 450(3.40)	21.7	0.0	22.9
	C_6H_{12}	–	–	–	–
3a[d]	DMSO	368(3.90), 448(3.06)	12.6	46.8	11.3
	EtOH	346(3.87), 436(3.43)	26.3	0.0	28.4
	$CHCl_3$	362(3.84), 446(3.11)	15.8	0.0	15.9
	C_6H_{12}	–	–	–	–

[a] $A_2/A_1 = x/(100 - x)$ where, A_1 = The absorbance of the phenol-imine isomer (π-π^*); A_2 = The absorbance of the keto-amine isomer (n-π^*); x = The percentage of keto-amine isomer.
[b] Acidic medium is attained by addition of CF_3COOH (1 mL) to the given solution (ligand concentration 5×10^{-5} mol L).
[c] Basic medium is attained by addition of NEt_3 (1 mL) to the given solution (ligand concentration 5×10^{-5} mol L).
[d] Not sufficiently soluble in C_6H_{12}.

observed at 1279-1272 and 1142–1030 cm^{-1}, respectively. The IR spectra of the sodium perchlorate complexes **1a–3a** feature split bands attributable to the asymmetric Cl–O stretching mode at ca. 1098–1091 cm^{-1} and the asymmetric Cl–O bending mode at ca. 626 cm^{-1}, suggesting that both bound and free anions are present [21]. Detailed IR data for the ligands and complexes are summarized in Table 3.

NMR spectra. The ^{1}H-NMR data and coupling constants of the ligands **1–4** and the complexes **1a–3a** are listed in Table 4. In the ^{1}H-NMR spectra of the ligands **1**, **2** and **4** the signals of the OH peaks are recorded as broad singlets at 13.90, 14.10 and 13.37 ppm, respectively, but in compound **3** this peak, interestingly enough, is observed at 6.70 ppm. This sharp singlet disappears by deuterium exchange. The azomethine (CH=N) protons are observed as singlets at 9.23, 9.21, 9.16 and 8.19 ppm for the ligands (**1-4**), respectively, showing that these ligands are dominantly in the phenol-imine form in $CDCl_3$. The crown ether protons (OCH_2–CH_2–) appear as multiplets between 3.64–4.34 ppm, respectively. The sodium complexes **1a–3a** are approximately the same as in the corresponding ligand spectra.

The ^{13}C-NMR data for the crown ether ligands **1–4** and their complexes **1a–3a** are given in Table 5. In the ^{13}C-decoupled NMR spectra of the ligands, eight crown ether carbons (C'_1–C'_8) are observed between 71.57–68.45 ppm. Methyl carbons of compounds **2**, **3**, **2a** and **3a** are at 24.75, 21.34, 29.50 and 21.06 ppm, respectively. The CH_2 signal of compound **4** is seen at 54.53 ppm.

MS spectra. In the EI mass spectra of the crown ether ligands **1–4** (Table 1) the respective molecular ion peaks are observed. Important fragments of compound **1** were found at *m/z* 371, 239 and 229, of compounds **2** and **3** at 385, 253 and 243, and of compound **4** at 374, 242 and 232 corresponding to the loss of [CH_3+2H], [$(CH_3CH_2O)_3$–CH_2], {[$(CH_2CH_2O)_3CH_2CH_2$]–H}, respectively. This fragmentation pattern proceeding by the loss of etheric chain segments is in accordance with the literature [4, 5, 22]. In the sodium

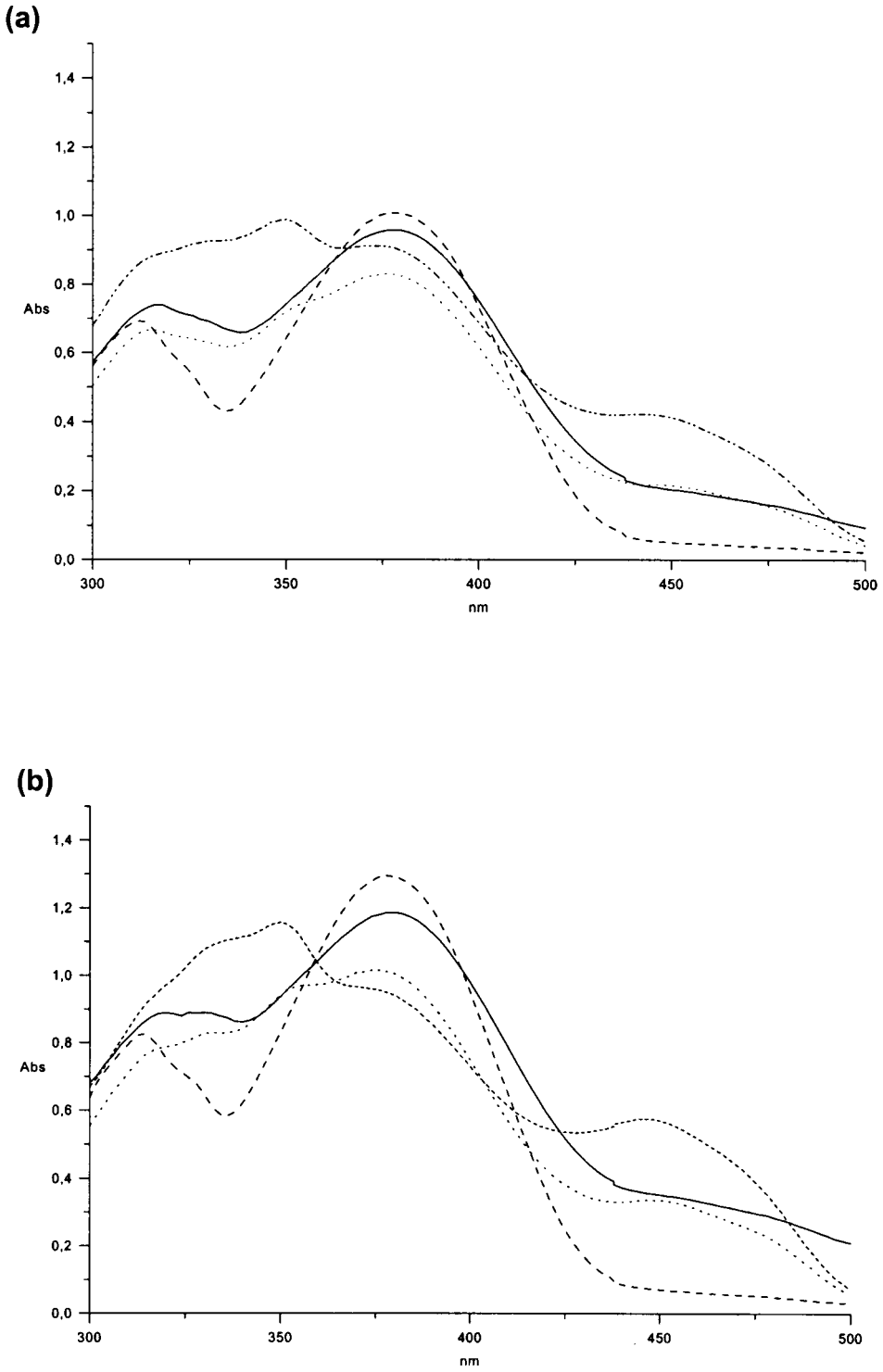


Figure 1. UV-Vis spectra showing solvent effect on compounds **1** (a) and **2** (b): DMSO ——, chloroform · · · · ·, ethanol - - - -, cyclohexane – – –; Schiff base concentration 5×10^{-5} mol L.

complex **2a**, a respective molecular ion peak at *m/z* 524 is not observed but only a peak at *m/z* 402 which corresponds to the free ligand **2**.

UV-Vis spectra. The UV-Vis spectra of the macrocyclic ligands **1–4** and complexes **1a–3a** were recorded in polar, acidic (CF_3COOH) and basic (Et_3N) media. The parameters of the spectra of the ligands and complexes in various solvents are listed in Table 6. Figures 1(a) and 1(b) show the corresponding UV-Vis spectra of compounds **1** and **2** in different solvents. Figures 2 and 3 show the acidic and basic effects of compound **2** in different solvents, respectively. The keto-amine tautomeric forms are present for the ligands **1–4** and complexes **1a–3a**. The spectra measured in non-polar solvent (C_6H_{12}) contain two bands at approximately 280 and 332–380 nm. These bands are due to π–π^* transitions.

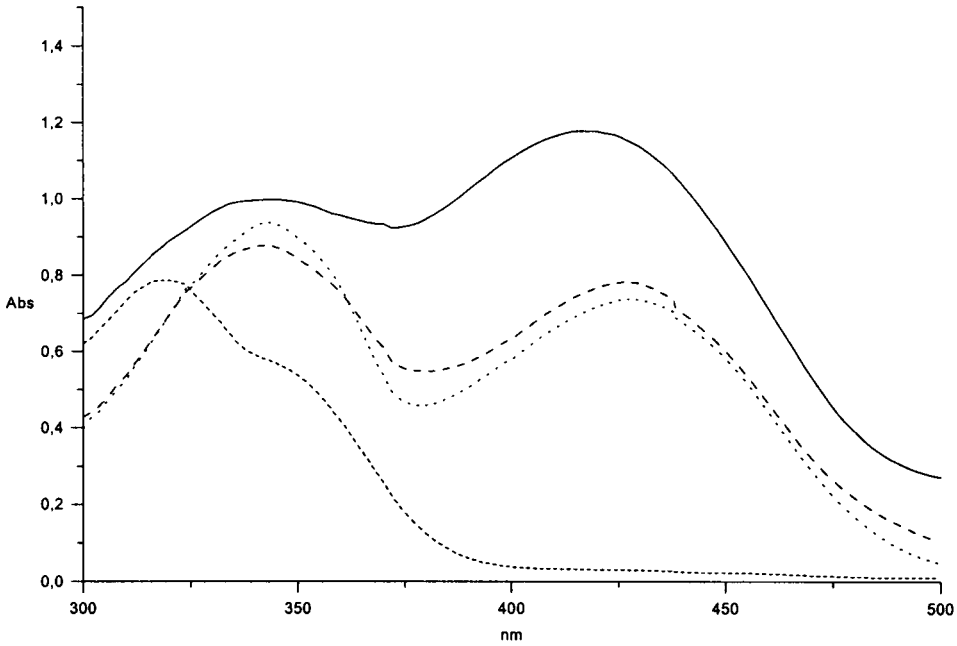


Figure 2. UV-Vis spectra showing acidic effect on compound **2**: DMSO ——, chloroform · · · · ·, ethanol - - - -, cyclohexane – – –; acidic media are satisfied by addition of CF_3COOH (1 mL) to the given solution ($c = 5 \times 10^{-}5$ mol L).

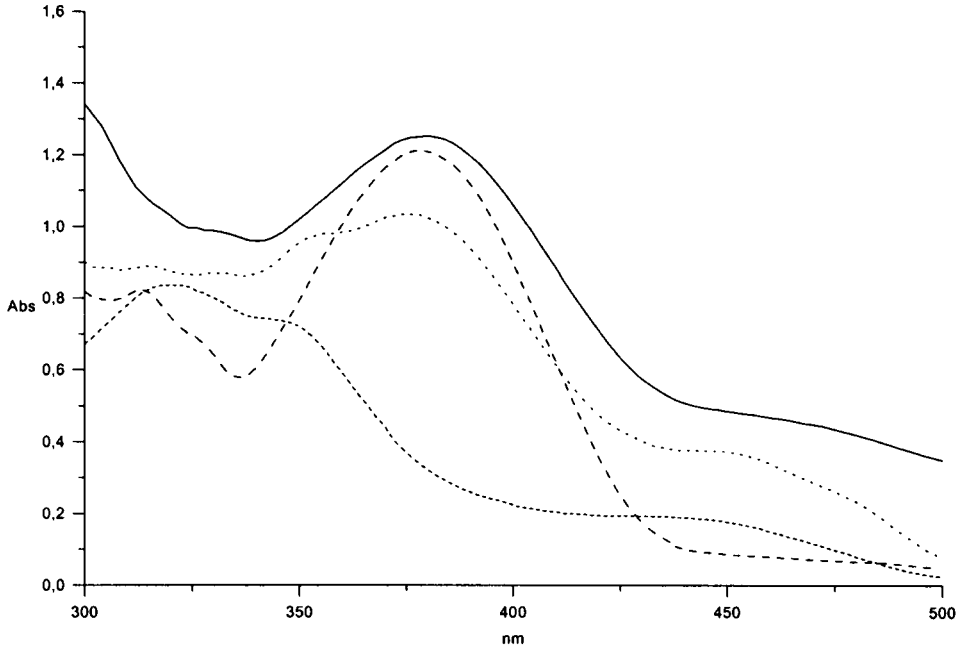


Figure 3. UV-Vis spectra showing basic effect on compound **2**: DMSO ——, chloroform · · · · ·, ethanol - - - -, cyclohexane: – – –; basic media are satisfied by addition of NEt_3 (1 mL) to the given solution ($c = 5 \times 10^{-5}$ mol L).

In polar solvents (DMSO, EtOH and $CHCl_3$), one additional band emerges approximately at 450 nm (n–π^*), which has logically been linked with the shift of the tautomeric equilibrium to the keto-amine form. There is a decrease in imino nitrogen basicity followed by a weakening of the intramolecular hydrogen bond (O–H· · ·N) and a decreased tendency of the tautomeric interconversion to keto-amine. For compounds **2** and **3**, containing a methyl substituent on the pyridine ring (on positions 4 and 6, respectively), the ratios of the keto-amine tautomers are higher values than the values of **1**. For solutions, the existence of both types of intramolecular hydrogen bonding in aldimine Schiff base ligands has been predicted from spectroscopic data [4, 5, 23–25] and confirmed in solid state by X-ray crystallography [23, 26–28]. In solutions, the tautomerism depends on the solvent polarity and the ability of the solvents to form hydrogen bonds. In EtOH, the ratios of the keto-amine tautomers of the ligands (**1–4**) and complexes (**1a–3a**) are higher than in DMSO and $CHCl_3$ which is possibly a concequence of the hydrogen bonding character of EtOH. In basic media, the keto-amine isomer is approximately the same as in the respective pure solvent media. Interestingly, when acid was

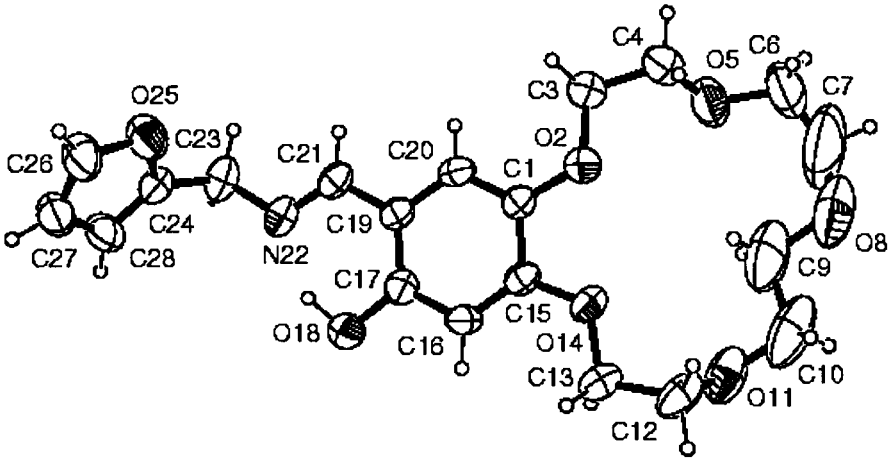


Figure 4. ORTEP-3 [42] drawing of compound **4** with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

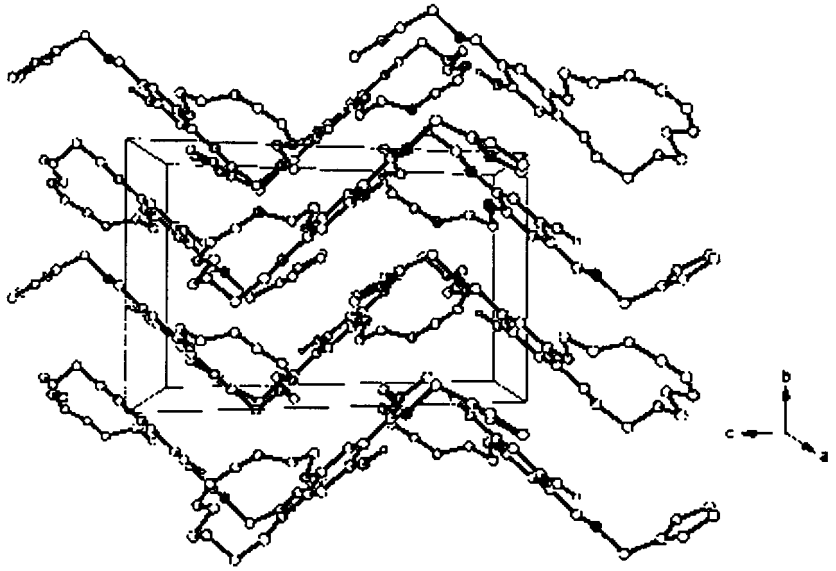


Figure 5. Packing diagram of compound **4**.

added to a non-polar solvent (C_6H_{12}) the keto-amine forms were observed for the ligands **1–3** but when the acid was added to apolar solvent (EtOH), the phenol-imine forms were dominant for all of the compounds. The influence of the complexation of sodium ion is dominant in decreasing the keto-amine isomer as expected. As known, sodium ion withdraws the electrons of the oxygen atoms in the macroring. Thus the electrons on the imine bond and N atom move toward the aromatic ring by decreasing the electron density on the N atom.

X-ray structural study

2-Hydroxy Schiff base ligands may have photochromic or thermochromic properties in the solid state by proton transfer from the hydroxyl oxygen atom to the imine nitrogen atom, reversibly. With respect to a classification reported [29], planar geometry of the unit cell contents is associated with thermochromism, while non-planarity is with photochromism. In the molecular systems, it is likely that a charge transfer occurs through overlapping intermolecular π-orbitals with proton transfer. Thus, the electrical properties may depend primarily on the intermolecular interactions causing the formation of the conductive thermochromic material in which the proton motion is basically correlated to the electron conduction, related with the molecular packing [30–32]. Moreover, 2-hydroxy Schiff bases have often been used as chelating ligands for obtaining transition and non-transition metal complexes [27, 33, 34]. In the solid state, they tend to form phenol-imine (N···H–O) or keto-amine (N–H···O) tautomerism, depending on the type of hydrogen bonding [35, 36]. Connected with these topics, the present structure determination of compound **4** was carried out to give a further proof of this particular behaviour of hydrogen bonding in the solid state and also to estimate the relative macrocyclic ring hole size in order to make a comparison with previously reported data [38–41].

Figure 4 shows a perspective view of the molecular structure of compound **4** including the numbering scheme of nonhydrogen atoms. The most relevant structural features of compound **4** are the intramolecular hydrogen bond between O(18) and N(22), and the conformation of the macroring, specified in more detail as follows.

The parameters of the O–H···N hydrogen bond [O(18)–H(18) 0.89(6), H(18)···N(22) 1.78(6), O(18)···N(22) 2.581(7) Å, O(18)–H(18)···O(22) 148.4(5)°] are typical of this type of intramolecular interaction, and unquestionably show that the compound is in the phenol-imine tautomeric form such as a similar Schiff base crown compound studied previously [26]. The intramolecular, O(2)···O(8) [4.629(6)], O(2)···O(11) [4.782(6)], O(5)···O(11) [5.051(5)], O(4)···O(14) [4.492(5)], O(8)···O(14) [4.782(6) Å] distances are indicative of the size of the ligand cavity. The relative macrocyclic inner-hole size, estimated as being twice the mean distance of the donor atoms from their centroid, is approximately 1.57 Å, using the modified covalent radius (0.76 Å) of the O_{sp^3} atoms as demonstrated in the literature [32]. To make a comparison, the corresponding macrocyclic inner hole size for unsubstituted 15-crown-5 is estimated to be 1.70–2.20 Å [40, 41], while hole sizes of 1.68 and 1.56 Å were found for two benzo-15-crown-5 Schiff bases corresponding to **4** [6, 26]. Hence, the inner hole size of **4** is in accordance with the reported values [43, 44]. The salicylidenimine ring system defined by the atoms C(1), C(15), C(16), C(17), C(19), C(20) and H(18), O(18), C(17), C(19), C(21), N(22) is nearly coplanar while the lateral furan ring and the salicylidenimine unit form an interplanar angle of 76.7(2). The ϕ_{CN} torsion angle [C(19)–C(21)–N(22)–C(23)] is 179.9(4)° showing that the configuration about the C(21)– N(22) bond is trans planar [*anti* (1E)].

In the packing, the molecules stack tightly with van der Waals and dipole–dipole interactions to form columns parallel to the a/c plane (Figure 5). This planar stacking may cause to the possibility of proton transfer by way of the hydrogen bonding in the ground state with a small amount of energy requirement, which is typical of thermochromic Schiff base ligands [29–32].

Acknowledgements

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