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MRC

Spectral Assignments and Reference Data

Synthesis and complete NMR characterization of 4-alkyl-2-(6-substituted-1,3-benzoxazol-2-yl)benzenols

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This paper describes the complete assignment of all carbons and hydrogens of several newly synthesized 6-substituted 2-(2-hydroxyaryl)benzoxazoles from 2,2′-dihydroxydiaryl Schiff bases by the use of two-dimensional NMR techniques.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; 2D techniques; 6-substituted 2-(2-hydroxyaryl)benzoxazoles

INTRODUCTION

Benzoxazole derivatives are used as dye lasers,[1] and zoxazolamine, a derivative of benzoxazole, is an effective sedative and muscle relaxant.[2] Some of these compounds have been tested for their anti tumor activities.[3] 2-(2-Hydroxyaryl)benzoxazoles assume importance because of their fluorescence and light-yield characteristics.[4] Although there are several methods of preparing benzoxazoles, oxidative ring closure of hydroxyimines is a popular method. During our investigations of the new precursors for side chain modified calixarenes, we synthesized several 4-alkyl-2[(5-substituted-2-hydroxyphenyl)iminomethyl]benzenols.[5] In this work, these 2-hydroxylimines were subjected to oxidative cyclization to obtain the corresponding benzoxazoles, which were fully characterized by a combined use of 1D and 2D NMR techniques.

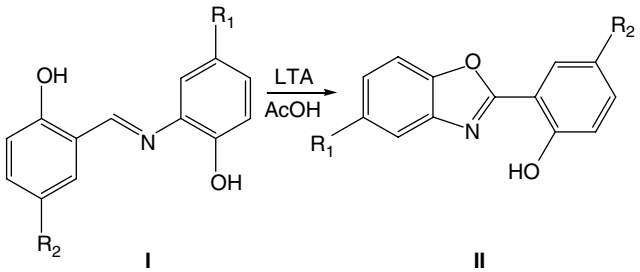
RESULTS AND DISCUSSION

The imines 4-alkyl-2-[(5-substituted-2-hydroxyphenyl) iminomethyl]benzenols (**I**) were prepared by the treatment of equimolar quantities of the corresponding aldehydes and amines.[5] The *N*-(2-hydroxyaryl)aldimines can be easily converted into benzoxazoles by oxidation with copper (II) acetate, lead tetraacetate[6] or silver oxide.[7] Among these reagents, lead tetraacetate is a common oxidizing agent and it was employed in this work.

Accordingly, a new series of benzoxazoles (**II**) were obtained in good yield by the treatment of the corresponding Schiff bases in acetic acid with one molar equivalent of lead tetraacetate (Scheme 1). The physical constants and the yields are given in Table 1. It should be noted that although there are two hydroxyl groups, both in the *ortho* positions of the C-aryl and N-aryl ring, it is the hydroxyl group in the N-aryl ring that is involved in cyclization, and that in C-aryl ring is not disturbed.

The synthesized compounds were fully characterized by NMR spectroscopy. The assignments of all the hydrogens and carbons were achieved by a systematic approach involving several 2D techniques such as H–H COSY, C–H COSY, DEPT, HMBC, NOESY, etc. The NMR data are given in Tables 2 (^{1}H) and 3 (^{13}C). The complete assignment for a representative benzoxazole, **IIa**, is presented here.

The 300 MHz ^{1}H NMR spectrum of **IIa** (Fig. 1) shows two doublets (J = 8.7 Hz) at 7.05 and 7.49 ppm. These must be due to H-3′and H-7. The highly shielded doublet at 7.05 ppm was assigned to H-3′, as it is *ortho* to the hydroxyl group. This is confirmed by the HMBC correlation of this peak with that at 156.96 ppm, which is easily assigned to C-2′ (see below). Consequently, the signal at 7.49 ppm is assigned to H-7. The two doublets of doublets at 7.46 ppm (J = 8.7, 2.4 Hz) and 7.40 ppm (J = 8.7, 1.8 Hz) are assigned between H-4′ and H-6 and the two doublets at 7.99 ppm



I **II**

	R_1	R_2
a	$C(CH_3)_3$	$C(CH_3)_3$
b	$C(CH_3)_3$	$CH(CH_3)_2$
c	$C(CH_3)_3$	$C(CH_3)_2CH_2CH_3$
d	$C(CH_3)_3$	CH_2CH_3
e	$C(CH_3)_3$	$C(CH_3)_2Ph$
f	$C(CH_3)_3$	Ph
g	$C(CH_3)_3$	Cl
h	$C(CH_3)_3$	Br
i	$C(CH_3)_3$	OCH_3
j	$CH(CH_3)_2$	$C(CH_3)_3$
k	$CH(CH_3)_2$	$CH(CH_3)_2$
l	$CH(CH_3)_2$	$C(CH_3)_2CH_2CH_3$
m	$CH(CH_3)_2$	$C(CH_3)_2Ph$
n	$CH(CH_3)_2$	Ph
o	$CH(CH_3)_2$	Cl
p	$CH(CH_3)_2$	Br
q	$CH(CH_3)_2$	OCH_3

Scheme 1

Table 1. Yields and melting-points of **II**

Compound	Melting-point (°C)	Yield (%)
IIa	162–163	81
IIb	116–117	77
IIc	120–121	75
IId	109–110	73
IIe	134–135	79
IIf	120–121	78
IIg	135–136	80
IIh	145–146	77
IIi	89–90	63
IIj	119–120	78
IIk	99–100	75
IIl	84–85	75
IIm	90–91	82
IIn	119–120	79
IIo	112–113	76
IIp	116–117	75
IIq	68–69	60

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Table 2. ^{1}H NMR data for **II**[a]

Compound	H-4 d	H-6 dd	H-7 d	H-3′ d	H-4′ dd	H-6′ d	R_1	R_2	OH
IIa	7.72 (1.8 Hz)	7.40 (8.7, 1.8 Hz)	7.49 (8.7 Hz)	7.05 (8.7 Hz)	7.46 (8.7, 2.4 Hz)	7.99 (2.4 Hz)	1.39 singlet	1.37 singlet	11.39
IIb	7.71 (1.8 Hz)	7.40 (8.7, 1.8 Hz)	7.48 (8.7 Hz)	7.04 (8.4 Hz)	7.28 (8.4, 2.1 Hz)	7.84 (2.1 Hz)	1.39 singlet	1.29(6H) doublet 2.90(1H) septet	11.36
IIc	7.73 (1.8 Hz)	7.43 (8.7, 1.8 Hz)	7.52 (8.7 Hz)	7.06 (8.7 Hz)	7.40 (8.7, 2.4 Hz)	7.94 (2.4 Hz)	1.40 singlet	0.72(3H) triplet 1.34(6H) singlet 1.68(2H) quartet	11.39
IId	7.72 (1.8 Hz)	7.41 (8.4, 1.8 Hz)	7.48 (8.4 Hz)	7.03 (8.7 Hz)	7.24 (8.7, 2.4 Hz)	7.81 (2.4 Hz)	1.39 singlet	1.27(3H) triplet 2.65(2H) quartet	11.35
IIe	7.73 (1.8 Hz)	7.42 (8.7, 1.8 Hz)	7.50 (8.7 Hz)	7.00 (8.7 Hz)	7.22 (8.7, 2.4 Hz)	7.97 (2.4 Hz)	1.40 singlet	1.74(6H) singlet 7.24–7.29 (5H)m	11.46
IIf	7.73 (1.5 Hz)	7.41 (8.7, 1.5 Hz)	7.49 (8.7 Hz)	7.16 (8.4 Hz)	7.63 (8.4, 2.4 Hz)	8.21 (2.4 Hz)	1.39 singlet	7.32(1H) *para* 7.44(2H) *ortho* 7.61(2H) *meta*	11.57
IIg	7.73 (1.8 Hz)	7.40 (8.7, 1.8 Hz)	7.50 (8.7 Hz)	7.04 (9.0 Hz)	7.33 (9.0, 2.7 Hz)	7.95 (2.7 Hz)	1.40 singlet	—	11.50
IIh	7.72 (2.1 Hz)	7.45 (8.4, 2.1 Hz)	7.48 (8.4 Hz)	6.96 (8.7 Hz)	7.43 (8.7, 2.7 Hz)	8.07 (2.7 Hz)	1.39 singlet	—	11.49
IIi	7.75 (1.5 Hz)	7.44 (8.7, 1.5 Hz)	7.52 (8.7 Hz)	7.05 —	7.05 —	7.48 —	1.41 singlet	3.87 singlet	11.15
IIj	7.55 (1.5 Hz)	7.22 (8.4, 1.5 Hz)	7.49 (8.4 Hz)	7.05 (8.7 Hz)	7.47 (8.7, 2.4 Hz)	7.99 (2.4 Hz)	1.31(6H) doublet 3.04(1H) septet	1.37 singlet	11.39
IIk	7.54 (1.8 Hz)	7.20 (8.4, 1.8 Hz)	7.46 (8.4 Hz)	7.03 (8.4 Hz)	7.28 (8.4, 2.1 Hz)	7.83 (2.1 Hz)	1.30(6H) doublet 3.02(1H) septet	1.28(6H) doublet 2.92(1H) septet	11.37
IIl	7.57 (1.5 Hz)	7.24 (8.4, 1.5 Hz)	7.51 (8.4 Hz)	7.06 (8.7 Hz)	7.41 (8.7, 2.4 Hz)	7.93 (2.4 Hz)	1.32(6H) doublet 3.05(1H) septet	0.72(3H) triplet 1.33(6H) singlet 1.68(2H) quartet	11.39

Table 2. (*Continued*)

Compound	H-4 d	H-6 dd	H-7 d	H-3′ d	H-4′ dd	H-6′ d	R_1	R_2	OH
IIm	7.55 (1.5 Hz)	7.21 (8.4, 1.5 Hz)	7.46 (8.4 Hz)	7.00 (8.7 Hz)	7.21 (8.7, 2.4 Hz)	7.96 (2.4 Hz)	1.30(6H) doublet 3.03(1H) septet	1.73(6H) singlet 7.24–7.28 (5H) m	11.46
IIn	7.55 (1.8 Hz)	7.21 (8.4, 1.8 Hz)	7.46 (8.4 Hz)	7.14 (8.4 Hz)	7.61 (8.4, 2.4 Hz)	8.18 (2.4 Hz)	1.36(6H) doublet 3.02(1H) septet	7.31(1H) *para* 7.41(2H) *ortho* 7.59(2H) *meta*	11.55
IIo	7.48 (1.8 Hz)	7.12 (8.4, 1.8 Hz)	7.39 (8.4 Hz)	6.94 (9.0 Hz)	7.24 (9.0, 2.4 Hz)	7.83 (2.4 Hz)	1.29(6H) doublet 2.99(1H) septet	—	11.40
IIp	7.51 (1.5 Hz)	7.21 (8.4, 1.5 Hz)	7.42 (8.4 Hz)	6.92 (8.7 Hz)	7.40 (8.7, 2.4 Hz)	8.02 (2.4 Hz)	1.30(6H) doublet 3.01(1H) septet	—	11.45
IIq	7.57 (1.5 Hz)	7.25 (8.4, 1.5 Hz)	7.51 (8.4 Hz)	7.03 —	7.03 —	7.46 —	1.32(6H) doublet 3.05(1H) septet	3.86 singlet	11.14

[a] Chemical shifts in ppm and coupling constants (Hz) in parentheses.

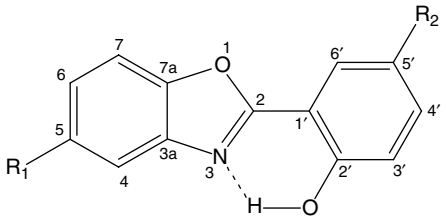

Figure 1. Orientation of hydroxyl group in **II**.

(J = 2.4 Hz) and 7.72 ppm (J = 1.8 Hz) to H-6′ and H-4. In the H–H COSY experiment the signal at 7.05 ppm exhibits a cross peak with the signal at 7.46 ppm, which in turn couples with the signal at 7.99 ppm. Similarly, the signal at 7.49 ppm couples with that at 7.40 ppm, which also couples with the signal at 7.72 ppm. This clearly shows that H-4′, H-6′, H-6 and H-4 appear at 7.46, 7.99, 7.40 and 7.72 ppm, respectively. The abnormal deshielding of H-6′ can be explained as a consequence of hydrogen bonding (see below).

As all the aromatic hydrogens have been unambiguously assigned, a C–H COSY experiment helps to assign all the CH carbons (Table 2). The signals at 35.41 and 34.66 ppm were assigned to the quaternary carbons of R_1 and R_2, respectively, as the former signal shows HMBC cross peaks with H-6 and H-4 and the latter with H-4′ and H-6′. Since the signal at 156.90 ppm couples with the OH proton at 11.39 ppm, H-3′, H-4′ and H-6′ in the HMBC spectrum, it is assigned to C-2′. Similarly, the signal at 142.65 ppm couples with the H-3′ proton, so it is C-5′. This carbon has HMBC connections with the methyl hydrogens at 1.37 ppm, and hence these are the R_2 methyls. The C–H COSY experiment indicates a connection between these hydrogens and the carbon at 31.88 ppm. The carbon at 110.35 ppm, which has HMBC correlations with OH and H-3′, must be C-1′. The deshielded carbon at 163.76 ppm can be assigned to C-2 as it is directly attached to both oxygen and nitrogen atoms, this assignment being corroborated by the fact that it has a cross peak with H-6′ in the HMBC spectrum. The carbons at 147.53 and 140.47 ppm can be fixed as C-7a and C-3a, respectively, as the former has HMBC correlations with H-6 and H-4 and the latter with H-7 and H-4. The signal at 148.92 ppm is due to C-5, since it couples with H-7 strongly in the HMBC spectrum. This carbon also exhibits an HMBC cross peak with the hydrogens at 1.39 ppm, proving that these are the R_1 methyl protons. The C–H COSY experiment makes the assignment complete as these methyl hydrogens have a correlation at 32.20 ppm.

The NOESY experiment helps to determine the orientation of the hydroxyl group in **II**. The position of the hydroxyl hydrogen suggests that strong intramolecular hydrogen bonding exists in the system. This hydrogen has NOESY contours only with H-3′ and H-4 and not with H-7, indicating that the hydroxyl group is closer to nitrogen than oxygen. Hence the structure shown in Fig. 1 represents the correct orientation of the hydroxyl group with the preferred hydrogen bonding to nitrogen. This also accounts for the abnormal deshielding of H-6′, which has to experience the anisotropy effect of the benzoxazole ring in a rotation-restricted planar arrangement.

It should be noted that in **IIi** and **IIq**, protons H-3′and H-4′ overlap to give a single signal at 7.05 ppm. Here the assignment of the respective carbons was made not from the C–H COSY spectrum, but by the fact that C-3′ has an HMBC correlation with the hydroxyl hydrogen. In the case of **IIf** and **IIn**, protons 4′ and 6′ are more deshielded (0.4 and 0.2 ppm, respectively, compared with other systems), which can be ascribed to the ring current anisotropy effect of the 5′-substituted phenyl ring. It is surprising that the ^{1}H-decoupled ^{13}C NMR spectrum of **IIj** has only three signals in the aliphatic region. The fact that the CH carbon of the isopropyl group and the quaternary carbon of the tert-butyl group have the same chemical shift value of 34.66 ppm, a rare observation, was established by an HMBC experiment.

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Table 3. ^{13}C NMR data for **II** (in ppm)

Compound	C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
IIa	163.76	140.47	116.15	148.92	123.38	110.15	147.53	110.35	156.96	117.41	131.35	142.65	123.63
IIb	163.63	140.46	116.16	148.90	123.39	110.12	147.53	110.68	157.24	117.63	132.29	140.29	124.68
IIc	163.79	140.49	116.13	148.92	123.34	110.13	147.52	110.36	156.86	117.33	131.85	140.96	124.41
IId	163.56	140.45	116.16	148.95	123.39	110.11	147.52	110.73	157.15	117.62	133.64	135.61	126.10
IIe	163.62	140.41	116.14	148.96	123.42	110.16	147.50	110.27	157.11	117.52	133.29	142.22	124.62
IIf	163.32	140.35	116.25	149.11	123.66	110.23	147.58	111.33	158.52	118.23	132.51	133.17	125.69
IIg	162.14	140.10	116.33	149.32	124.02	110.31	147.53	112.10	157.51	119.26	133.53	124.75	126.67
IIh	161.99	140.07	116.32	149.29	124.02	110.30	147.51	112.67	157.95	119.64	136.31	111.64	129.60
IIi	163.25	140.44	116.24	149.08	123.56	109.97	147.52	110.66	153.52	118.77	121.66	152.89	110.15
IIj	163.75	140.66	116.86	146.58	124.49	110.48	147.87	110.32	156.94	117.39	131.36	142.66	123.63
IIk	163.63	140.65	116.86	146.59	124.51	110.45	147.86	110.66	157.24	117.63	132.31	140.29	124.68
III	163.78	140.68	116.85	146.58	124.46	110.46	147.86	110.34	156.84	117.32	131.88	140.95	124.41
IIm	163.66	140.65	116.88	146.63	124.56	110.53	147.87	110.29	157.18	117.58	133.33	142.25	124.67
IIn	163.32	140.45	116.96	146.76	124.76	110.56	147.91	111.31	158.53	118.23	132.51	133.15	125.67
IIo	162.03	140.24	116.99	146.84	125.05	110.57	147.78	111.95	157.49	119.18	133.44	124.68	126.57
IIp	161.95	140.24	117.01	146.88	125.09	110.60	147.80	112.60	157.95	119.61	136.28	111.62	129.56
IIq	163.24	140.63	116.94	146.72	124.66	109.96	147.86	110.63	153.46	118.76	121.66	152.88	110.48

For **IIa**	R_1: $\underline{C}(CH_3)_3$ 35.41, $C(\underline{C}H_3)_3$ 32.20,	R_2: $\underline{C}(CH_3)_3$ 34.66, $C(\underline{C}H_3)_3$ 31.88
For **IIb**	R_1: $\underline{C}(CH_3)_3$ 35.41, $C(\underline{C}H_3)_3$ 32.19,	R_2: $\underline{C}H(CH_3)_2$ 33.77, $CH(\underline{C}H_3)_2$ 24.54
For **IIc**	R_1: $\underline{C}(CH_3)_3$ 35.40, $C(\underline{C}H_3)_3$ 32.18,	R_2: $\underline{C}(CH_3)_2CH_2CH_3$ 37.85, $C(\underline{C}H_3)_2CH_2CH_3$ 28.95, $C(CH_3)_2\underline{C}H_2CH_3$ 37.25, $C(CH_3)_2CH_2\underline{C}H_3$ 9.56
For **IId**	R_1: $\underline{C}(CH_3)_3$ 35.40, $C(\underline{C}H_3)_3$ 32.18,	R_2: $\underline{C}H_2CH_3$ 28.41, $CH_2\underline{C}H_3$ 16.18
For **IIe**	R_1: $\underline{C}(CH_3)_3$ 35.41, $C(\underline{C}H_3)_3$ 32.18,	R_2: $\underline{C}(CH_3)_2$Ph-42.86, $C(\underline{C}H_3)_2$Ph-31.26, $C(CH_3)_2\underline{Ph}$-*ipso*-150.81, Others-126.18, 127.12, 128.52
For **IIf**	R_1: $\underline{C}(CH_3)_3$ 35.44, $C(\underline{C}H_3)_3$ 32.19,	R_2: $\underline{Ph}$-*ipso* 140.47, *ortho* 129.28, *meta* 127.11, *para* 127.47
For **IIg**	R_1: $\underline{C}(CH_3)_3$ 35.43, $C(\underline{C}H_3)_3$ 32.14,	R_2: -
For **IIh**	R_1: $\underline{C}(CH_3)_3$ 35.43, $C(\underline{C}H_3)_3$ 32.15,	R_2: -
For **IIi**	R_1: $\underline{C}(CH_3)_3$ 35.41, $C(\underline{C}H_3)_3$ 32.16,	R_2: $O\underline{C}H_3$ 56.35
For **IIj**	R_1: $\underline{C}H(CH_3)_2$ 34.66, $CH(\underline{C}H_3)_2$ 24.84	R_2: $\underline{C}(CH_3)_3$ 34.66, $C(\underline{C}H_3)_3$ 31.87
For **IIk**	R_1: $\underline{C}H(CH_3)_2$ 34.66, $CH(\underline{C}H_3)_2$ 24.84	R_2: $\underline{C}H(CH_3)_2$ 33.77, $CH(\underline{C}H_3)_2$—24.54
For **III**	R_1: $\underline{C}H(CH_3)_2$ 34.65, $CH(\underline{C}H_3)_2$ 24.83	R_2: $\underline{C}(CH_3)_2CH_2CH_3$ 37.85, $C(\underline{C}H_3)_2CH_2CH_3$ 28.95, $C(CH_3)_2\underline{C}H_2CH_3$ 37.25,$C(CH_3)_2CH_2\underline{C}H_3$ 9.55
For **IIm**	R_1: $\underline{C}H(CH_3)_2$ 34.67, $CH(\underline{C}H_3)_2$ 24.86	R_2: $\underline{C}(CH_3)_2$Ph 42.89, $C(\underline{C}H_3)_2$Ph 31.29, $C(CH_3)_2\underline{Ph}$-*ipso* 150.84, Others 126.21, 127.16, 128.57
For **IIn**	R_1: $\underline{C}H(CH_3)_2$ 34.68, $CH(\underline{C}H_3)_2$ 24.86	R_2: Ph- *ipso* 140.55, *ortho* 129.28, *meta* 127.10, *para* 127.47
For **IIo**	R_1: $\underline{C}H(CH_3)_2$ 34.62, $CH(\underline{C}H_3)_2$ 24.79	R_2: -
For **IIp**	R_1: $\underline{C}H(CH_3)_2$ 34.63, $CH(\underline{C}H_3)_2$ 24.81	R_2: -
For **IIq**	R_1: $\underline{C}H(CH_3)_2$ 34.65, $CH(\underline{C}H_3)_2$ 24.82	R_2: $O\underline{C}H_3$ 56.33

The mass spectral fragmentation of **IIa** shows a prominent M − 15 peak as the base peak, characteristic for systems with tert-butyl or isopropyl substituents. It is interesting that this fragment ion loses oxygen and CO units to give M − 31 and M − 43 peaks, respectively. It should be noted that **IIh** does not have the M − 31 peak, although it has the other two prominent peaks shown by **IIa**.

EXPERIMENTAL

The melting-points are uncorrected. The ^{1}H, ^{13}C and related 2D NMR spectra were recorded on a Bruker 300 MHz (UltraShield) NMR spectrometer at room temperature. The ^{1}H NMR spectra were measured for an ~0.03 M solution in $CDCl_3$ and ^{13}C NMR spectra for an ~0.05 M solution in $CDCl_3$ with TMS as internal reference for both ^{1}H and ^{13}C. The one- and two-dimensional NMR spectra were recorded using the Bruker icon NMR software. For ^{13}C NMR spectra, a pulse angle of 37.5° (5 μs), an acquisition time of 0.75 s and a repetition time of 3.72 s were used. The mass spectra were recorded on a Finnigan GC–MS instrument.

Preparation of 4-alkyl-2[(5-substituted-2-hydroxyphenyl)iminomethyl]benzenol

A mixture of 0.01 mol of aldehyde and 0.01 mol of amine was refluxed in 100 ml of alcohol for 1 h. The pure Schiff base **I** became solidified on cooling after concentrating the solvent.

Preparation of 4-alkyl-2-(6-substituted-1,3-benzoxazol-2-yl)benzenol

A 0.01 mol amount of the Schiff base **(I)** was stirred in acetic acid (50 ml) with 0.01 mol of lead tetraacetate. The reaction was completed within 10 min. The pure benzoxazole **II** was isolated after dilution, extracted with chloroform followed by silica column chromatography, and crystallized from ethanol.

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