Synthesis and ^{1}H NMR Structural Analysis of 11-aryl/heteroarylnaphtha[2,1-*b*]furans: X-ray Crystal Structure of 11-(4'-pyridyl)naphtho[2,1-*b*]furan

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Synthesis of biaryl type systems, 11-aryl/heteroarylnaphtho[2,1-*b*]furans **8-11** has been described with a view to studying the conformational orientation of C-11 aryl/heteroaryl groups. Synthesis of **8-11** was accomplished by a two-step sequence involving O-alkylation of 2-naphthol with appropriate halo-ketones **2-4**, followed by cyclization of the resulting naphthoxy-ketones **5-7** with methanesulphonic acid. The structures of **8-11** are based on detailed 2D NMR spectral analysis. The H8 in these compounds is not subject to significant anisotropic upfield shielding effects. The slightly upfield chemical shift of H8 in molecules **9-11**, relative to **8** has been correlated with the electron density at C17 and C8 positions. While molecular modeling indicated dihedral angle (φ) between the C11 aryl/heteroaryl groups and the naphthofuran plane to be in the range of 70-60° in **8-10**, a single X-ray crystal structural analysis of 11-(4'-pyridyl)naphtho[2,1-*b*]furan **10** indicated (φ) of 64.36°. In view of significant deviations from the orthogonal oreintation, the absence of any significant anisotropic shielding in **8-11** is not entirely unexpected.

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The biaryl structural motif is of fundamental importance to investigate atropisomerism [1]. The torsional angle between the aryl-aryl bond is believed to play a key role in controlling photophysical and biological activities associated with biaryl systems [2]. In this context, modern techniques which include ^{1}H NMR and X-ray crystal structural analysis have been extensively used to probe the orientation and molecular structures of a variety of biaryl systems [3-6]. Further impetus to study biaryls stems from the presence of biaryl core in a large number of biologically active molecules and due to ever increasing demand of axially chiral biaryls as asymmetric catalysts [7-11]. Moreover, certain complex biaryls exemplified by 1,8-diaryl/heteroaryl naphthalenes are of interest to study their conformations, through-space aryl-aryl interactions and nonlinear optic properties [12-15].

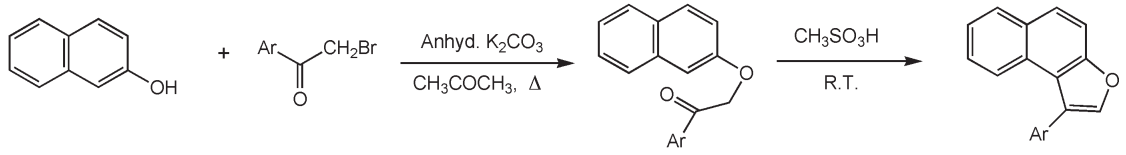
Though, a number of 11-alkyl/aryl naphtho[2,1-*b*]furans have been described in the literature [16-22], surprisingly only limited information is currently available on their spectral properties or molecular structures [23]. To our knowledge, no report dealing with the conformational orientation in C-11 aryl naphtho[2,1-*b*]furans has appeared to date. In continuation of our interest on conformational implications of biaryl systems on spectral properties [24-25], we deemed it of interest to examine the conformational orientation in 11-aryl/heteroaryl naphtho[2,1-*b*]furans. Herein, we report the synthesis and detailed ^{1}H NMR spectral analysis of 11-aryl/heteroarylnaphtho[2,1-*b*]furans **8-11** containing π-rich anisyl and π-deficient *p*-nitrophenyl and 4-pyridyl/pyridinium groups. In addition, a single X-ray crystal structural analysis of **10** is also reported which support the conclusions reached by ^{1}H NMR spectral interpretations on molecules **8-11**.

The synthetic strategy used towards **8-10** is depicted in Scheme 1 and is based on a two step sequence involving O-alkylation of 2-naphthol **1** with appropriate aryl haloketones **2-4**, followed by ring closure under acid catalysis. The methodology is an extension of that reported in the literature for the synthesis of 11-methylnaphtho[2,1-*b*]furan [19]. Towards our first target, namely 11-(4'-methoxyphenyl)naphthofuran **8**, 2'-bromo-4-methoxyacetophenone **2** was reacted with 2-naphthol under anhyd K_2CO_3/acetone condition to afford O-naphthoxy derivative **5** in 60% yield as a colourless solid. When treated with neat methanesulphonic acid at room temperature, compound **5** cyclized to provide the desired compound naphthofuran **8** as a colourless solid in 45% yield. The structure **8** is fully supported by elemental composition and spectral data.

The synthesis of **9** was likewise carried out by reacting 2-naphthol with 2'-bromo-4-nitroacetophenone **3** to give **6** in 30% yield. The cyclization of **6** with methanesulphonic acid produced the desired 11-(4'-nitrophenyl)naphtho[2,1-*b*]furan **9** as a pale yellow solid in 55% yield. In order to prepare the pyridyl analog **10**, we carried out the reaction of known 2'-bromo-4-pyridylketone hydrobromide salt **4** with 2-naphthol to form **7**, which on treatment with methanesulphonic acid gave after SiO_2 column purification, the desired naphthofuran **10** in 40% yield. Further, in order to enhance the π-acceptor property of the pyridyl ring, we converted **10** into the corresponding N-methyl salt by reacting with an excess of CH_3I in dry tetrahydrofuran solvent. The required N-quaternized naphthofuran **11**, mp 240-42 °C was obtained in quantitative yield.

For naphthofurans **8-11**, which belong to biaryl type systems, we expect the C-11 aryl/heteroaryl group to be

Scheme 1

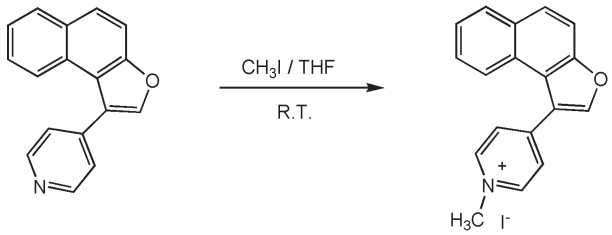


1

2: 4-MeO-C_6H_4-
3: 4-O_2N-C_6H_4-
4: 4-pyridyl

5: 4-MeO-C_6H_4-
6: 4-O_2N-C_6H_4-
7: 4-pyridyl

8: 4-MeO-C_6H_4-
9: 4-O_2N-C_6H_4-
10: 4-pyridyl



10 **11**

Synthesis of 11-aryl/heteroaryl naphtho[2,1-*b*]furans **8-11**

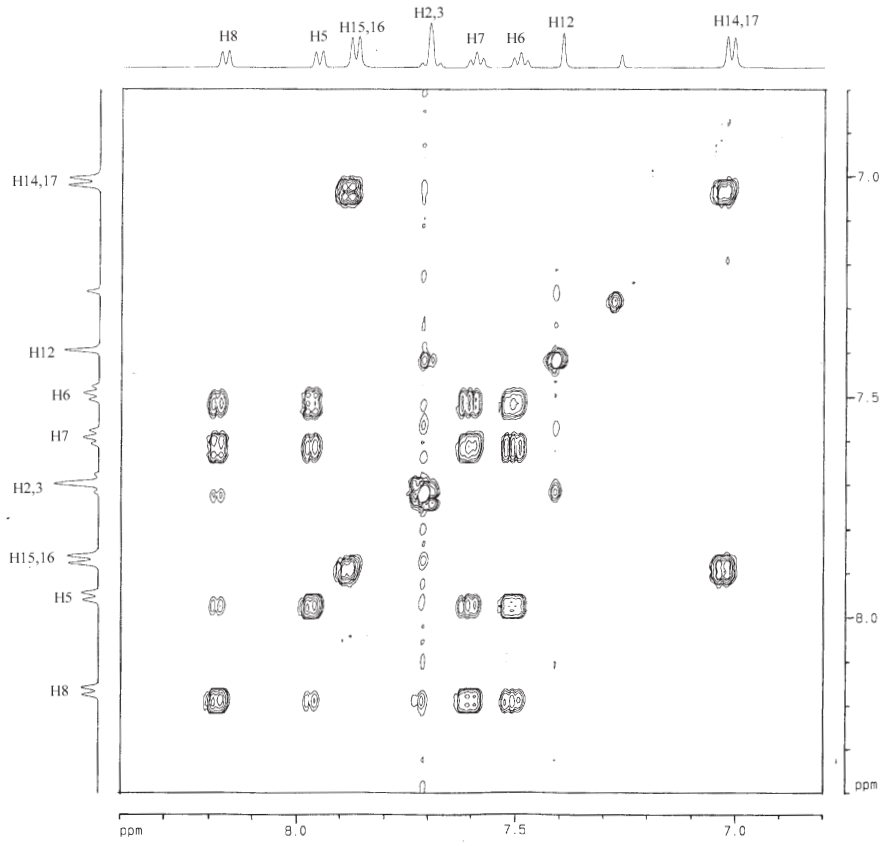
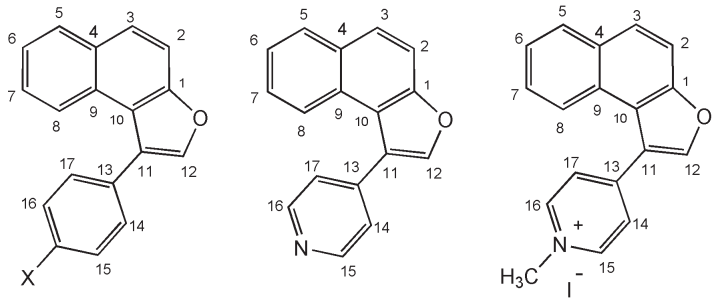


Figure 1. COSY spectrum of **8.** Assignment of protons are depicted in both projection

Table 1

^{1}H NMR data (δ, $CDCl_3$, 500 MHz) of **8-11** Based on COSY and NOESY spectra [a]



8: X= OCH_3 **10** **11**
9: X= NO_2

Type of H	**8**	**9**	**10**	**11**
H-12	7.39 (s,1H)	7.76 (s, 1H)	7.73 (s, 1H)	8.04 (s, 1H)
H-2	7.60 (d, 2H) [b]	7.73 (d,1H)	7.62 (d,1H)	7.72 (d,1H)
H-3		7.80 (d,1H)	7.83 (d,1H)	7.83 (d,1H)
H-5	7.95 (d,1H)	7.89 (d, 1H)	7.95 (d, 1H)	7.87 (d, 1H)
H-6	7.48 (t,1H)	7.41 (t, 1H)	7.42 (t, 1H)	7.52 (t, 1H)
H-7	7.59 (t,1H)	7.49 (t, 1H)	7.49 (t, 1H)	7.60 (t, 1H)
H-8	8.16 (d,1H)	7.98 (d, 1H)	7.95 (d, 1H)	7.93 (d, 1H)
H-14 and H-17	7.86 (d, 2H)	7.81 (d, 2H)	7.57 (d, 2H)	8.23 (d, 2H)
H-15 and H-16	7.01 (d, 2H)	8.39 (d, 2H)	8.78 (d, 2H)	9.22 (d, 1H)
				N-CH_3 4.75 (s, 3H)

[a] For the parent naphtho[2,1-*b*]furan, the H8 appears at δ 8.14 [26]. [b] overlapping double doublets.

twisted out of the plane of naphthofuran on account of the steric congestion. On the other hand, π-conjugative tendency between the C11 aryl/heteroaryl groups and the naphthofuran framework would tend to enforce coplanarity in **8-11**. Accordingly, depending upon the angle of twist, we expect the H8 in **8-11** to experience varying degree of anisotropic shielding ring current effect. Consequently, the magnitude of upfield shift of H8 in comparison with a reference standard without C-11 aryl group might provide a qualitative indication on the probable orientation of C-11 aryl substituents with respect to the plane of the naphthofuran ring. With this proposition in mind, we carried out a detailed ^{1}H NMR analysis of naphthofurans **8-11** and the data are compiled in Table 1.

The resonance assignments for various protons are based on their chemical shift positions, coupling constants and 2-D ^{1}H NMR spectral analysis. For comparison, a partial ^{1}H NMR spectral assignment for the parent naphtho[2,1-*b*]furan, based on the literature data and our independent analysis by COSY and NOESY spectra is also given in the footnote of the Table 1. It is expected that protons H5, H6, H7, and H8 should form an ABMX type systems, while H2 and H3 should constitute either an AB or AX system. Further, in analogy to literature report [23] and on account of the 1,10 fusion with the furan ring, protons H2 and H3 should resonate at relatively higher fields than H5-H8 protons. To start with, for the case of **8** simple ^{1}H NMR spectrum allowed definitive assignment only for the anisyl protons (doublets at δ 7.86 and δ7.01, *J*= 7 Hz) and the C12 furan ring proton which is observed as a singlet at δ 7.39. The resonances for the remaining protons are complex, and their assignments required the application of 2-D NMR techniques. Thus, using a combination of COSY and NOESY spectra, we have successfully assigned individual protons for **8-11** systems. For illustration, COSY and NOESY spectra of 11-(4'-methoxyphenyl) naphtho[2,1-*b*]furan **8** are depicted in Figures 1 and 2, respectively. From the COSY spectrum, we can discern a superimposable pair of higher field doublets at δ 7.60 (2H), which are assignable to mutually coupled H2 and H3 protons. Among the ABMX system comprising of H5-H8 protons, the COSY spectrum revealed connectivities between a relatively higher field doublet at δ 8.16 with the triplet centered at δ 7.59, whereas a lower field doublet at δ 7.95 can be correlated with the triplet at δ 7.48. From the NOESY spectrum, an NOE interaction between the doublet at δ 7.95 with the resonance at δ 7.60 is seen which is attributable to through-space interaction between the *peri* H5 and H3 protons. Considering higher electron density at C3 compared to C5 position [24], we can assign the lower field doublet at δ 7.95 to H5 and higher field resonance at δ 7.60 to H3 proton. With the

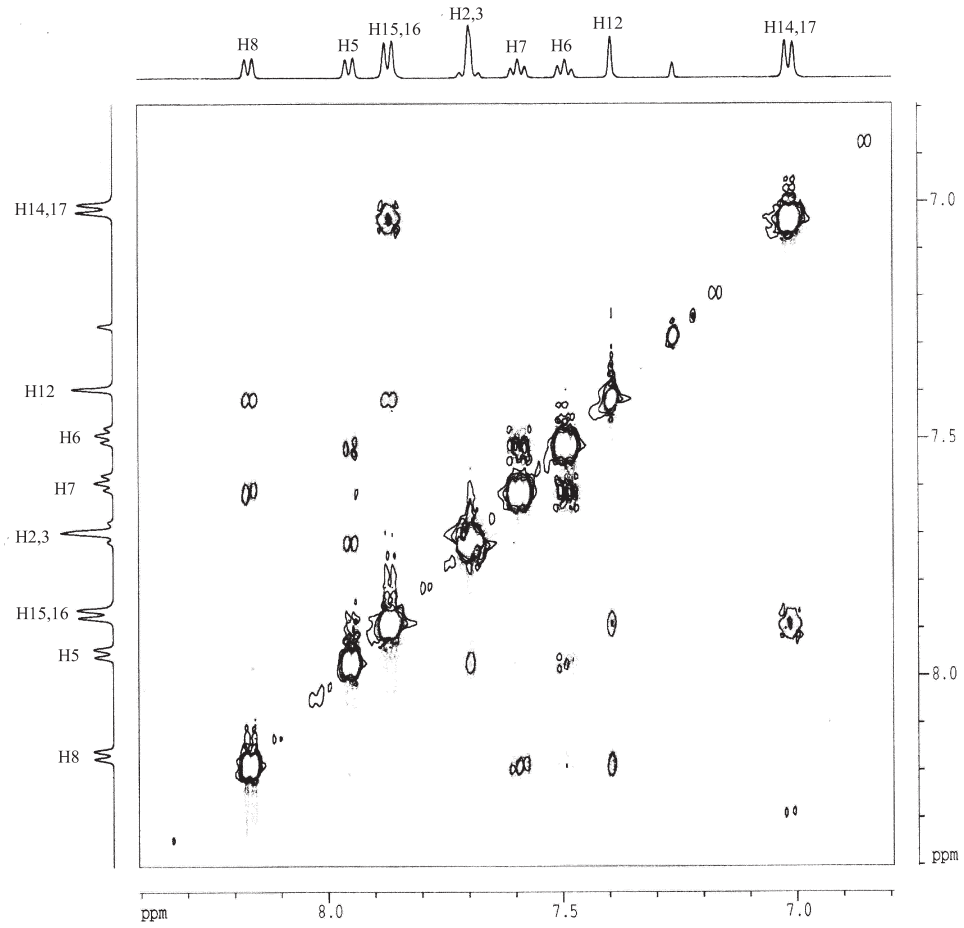


Figure 2. NOESY spectrum of **8**. Assignments are depicted in both projection, mixing time, t_m=278ms

assignment of H5 thus having been secured, we can now conveniently return to the COSY spectrum to resolve the assignments to remaining H6-H8. Thus, using the off-diagonal connectivity, we can safely assign the doublet at δ 8.16 to H8 proton, whereas triplets at δ 7.59 and δ 7.48 are coupled respectively to H7 and H6 protons. The sequence of chemical shifts in the ABMX has been found in the order $\delta_8>\delta_5>\delta_7>\delta_6$ which is in agreement with that reported for some 3-naphtho[2,1-*b*]furan carboxylic acid and its derivatives [23]. Curiously, the chemical shift position of H8 in **8** which is observed at δ 8.16 is nearly at the same value as reported for the parent naphtho[2,1-*b*]furan system at δ 8.14 [26]. This observation probably implies the absence of detectable diamagnetic upfield shielding effect in **8**.

For remaining molecules **9-11**, assignments of different protons were likewise made on the basis of COSY and NOESY spectral analysis. For **9-11** containing electron deficient *p*-nitrophenyl or pyridyl/pyridinium rings at the C-11 position, the effect of electron withdrawal is clearly reflected in the downfield shift of the H12 proton (δ 7.73 to 8.04) compared to position of the corresponding proton in the anisyl compound **8** at δ 7.39. For the case of pyridinium naphthofuran **11**, the H12 appears further down field at δ 8.04 relatively to the pyridine analog **11** (H12 appears at δ7.73). This is consistent with the enhanced electron deficiency of the pyridinium ring that causes greater electron withdrawal from the furan ring to result in relatively greater downfield shift of H12 proton in **11**. For remaining naphthaleno protons of **9-11**, a trend similar to that seen for the anisyl naphthofuran **8** was observed with no significant differences being noted in the chemical shift positions.

For the case of **9-11** carrying π-deficient rings at the C-11 position, we expected the H8 proton to experience relatively less anisotropic shielding (and consequently downfield shifts) compared to that observed in the π-rich molecule **8**. However, contrary to our expectation, the H8 proton in **9-11** was found to resonate at slightly higher fields in the range of δ 7.93 to 7.98 compared to δ 8.16 observed for the case of **8**. In order to shed light on this seemingly unusual result, we carried out electron density calculations and conformational energy minimization on **8-10** [27]. We excluded **11** from the

energy minimization on account of positional uncertainty of the iodide ion. The computed electron density on selected atoms in systems **8-10** is depicted in Figure 3. Since, the C17 of the aryl/heteroaryl group is spatially proximate to the H8 proton (for numbering scheme, see Table 1) the electron density on this particular carbon is expected to contribute maximally to the ring anisotropic effect. As shown in Figure 3, the electron density on the C17 carbon in molecules **8**-**10** is found to be in the order **8>9>10**. Thus, working on the reasonable assumption that and pyridyl rings displayed lower φ of *ca*. 60°. We propose that the lower degree of twist and relatively higher electron density at the C17 in molecules **9** and **10** in comparison to **8** could be a consequence of resonance charge delocalization from the π-rich naphthofuran ring to π-deficient C11 rings in the former systems. The downfield position of the H12 proton in **9-11** (δ 7.73 to 8.04) compared to that observed for **8** at δ 7.39 fully supports this suggestion.

For **10**, which gave suitable crystals, we carried out its single crystal X-ray structural analysis in order to evaluate

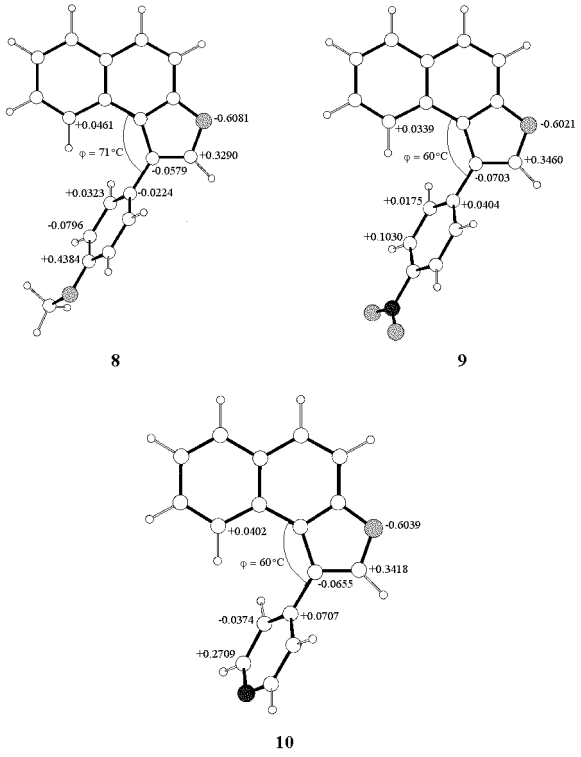


Figure 3. Computed electron density and dihedral angles of **8-10**

the higher the magnitude of electron density on C17 the greater would be the anisotropic effect, the upfield shielding effect experienced by H8 should then follow the order **8>9>10**. Consistent with this proposition, the resonance of the H8 proton indeed appears upfield in the same order. Furthermore, the chemical shift position of H8 (δ **8>9>10**) is also in accord with the decreasing order of electron density at the C8 position in these molecules. Thus, on ground of electron density on C8 and C17 positions, the observed higher field resonance of H8 in **9-10** (in analogy, also in **11**) relative to **8** appears reasonable. Geometry minimization [27] revealed an interesting insight into the conformations of molecules **8-10**. While, **8** carrying a π-donor anisyl ring at the C-11 position possessed the dihedral angle (φ) of *ca*. 71°, molecules **9** and **10** with the π-deficient 4-nitrophenyl its molecular structure [28]. The unit cell of **10** was identified as monoclinical and structure was solved by direct method with S.I.R-97. The crystal data and detail of structure determination are given in Table 2. An ORTEP plot of the molecule together with key structural features are presented in the Figure 4. Firstly, the torsion angles of -176.38° and 4.8° for atoms encompassing [C7,C8, C9,C10] and [C8,C9,C10,C11] indicate that the naphthofuran framework itself is almost planar with a slight upward bending at the C4-C9 fusion, while the C1-C10 fusion shows a slight downward curve. The most important revelation from the X-ray structure comes from the torsion angle of 64.36° encompassing C12, C11, C13, and C14. Molecular modeling had revealed a close value of 60° for this systems. This is the dihedral angle φ between

Table 2

Summary of Crystallographic Data and Refinement Details

Empirical formula	$C_{17}H_{11}NO$
Formula mass	245.28
Crystal color and habit	colorless,block
Crystal size[nm]	$0.47 \times 0.41 \times 0.22$
Crystal system	monoclinic
a [A°]	7.4126(4)
b [A°]	7.724(1)
c [A°]	21.766(1)
β [°]	94.787(1)
V [A°3]	1241.88(11)
Z	4.0
$\rho_{calcd.}$ [g/cm^3]	1.312
F(000)	512
μ [cm^{-1}]	0.82 (Mo-Kα)
$2\theta_{max}$ [°]	56.56 (I > 3.0σ)
No. of reflections	3080
R_{int}	0.0159
No. of parameters	216
R	0.0409
R_w	0.1136
GOF	1.038

the planes of the naphthofuran and the pyridine ring. The deviation from the orthogonal orientation result in minor diamagnetic shielding effects as also borne out by our ^{1}H NMR interpretation of **8-11**. Whereas the sp^2 bond angle, C3-C4-C5 at 120.46° is almost normal, the bond angles for C10-C11-C13 and C9- C10- C11 are 128.6° and 135.66°, respectively. These angles are substantially larger than the normal value of 120°. Relative larger bond angles probably arise in order to accommodate molecular strain imposed by the presence of C-11 pyridyl group. In addition, the σ bond length C11-C13 between the pyridine and the naphthofuran ring is slightly longer at 1.48 Å compared with the normal value of *ca.*1.44 Å. Increase in this bond length could at least in part be due to the tendency to minimize the steric interaction from the naphthyl residue and the C8 hydrogen atom. It appears that besides the steric factor that would maximize the torsion, an opposing interaction namely the π-conjugative tendency between the C-11 aryl/heteroaryl groups and the naphthofuran ring would tend to enforce coplanarity. The observed and calculated dihedral angles reflect a balance between steric and electronic factors. As a consequence of π-delocalisation, the reduced twists, in donor acceptor type molecules **9-10** relative to **8** is understandable.

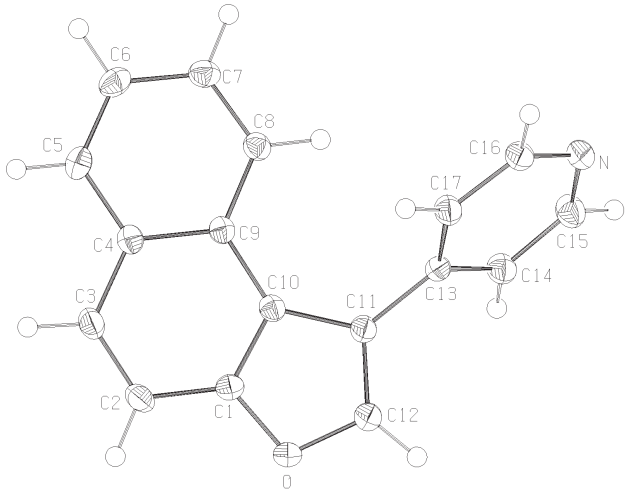


Figure 4. ORTEP Plot of the X-ray crystal structure of **10**. Selected (i) interatomic distances (Å): C(11)-C(13), 1.479 (14); C(10)-C(11), 1.448(13);C(10)-C(9), 1.429(13); C(11)-C(12), 1.356(15); (ii) bond angles (°): C(3)-C(4)-C(5), 120.46; C(8)-C(9)-C(10), 124.38; C(9)-C(10)-C(11), 135.66; C(10)-C(11)-C(13), 128.67; C(12)-C(11)-C(13), 125.47: (iii) torsion angle (°): C(8)-C(9)-C(10)-C(11), 4.78; C(10)-C(11)-C(13)-C(17), 60.33; C(10)-C(11)-C(13)-C(14), -120.97; C(7)-C(8)-C(9)-C(10), -176.38; C(12)-C(11)-C(13)-C(14), 64.36; C(12)-C(11)-C(13)-C(17), -114.34.

In summary, we have reported the synthesis and structural characterization of naphthofurans **8-11**. 2D NMR spectral analysis allowed complete assignments of various protons of these molecules. Minor upfield shielding effects for the H8 were observed in **9-11** relative to **8** are consistent with higher electron density on C8 and C17 positions in **9-11** relative to **8**. Molecular modeling and the X-ray crystal structural analysis revealed dihedral angles that are deviated from the orthogonal orientation required to observe significant anisotropic shielding in **8-11**. Work is currently in progress to evaluate biological activity and nonlinear optic properties of naphthofurans **8-11**.

EXPERIMENTAL

The chemicals and solvents for synthesis and column chromatography were purchased from S/D Fine Chemicals and Merck (India) and used as received. Melting points (uncorrected) were determined on a Gallenkamp melting point apparatus. IR spectra were recorded on a Shimadzu FTIR-420 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker-AMX-500 spectrometer with TMS as an internal standard. Elemental analyses were performed by the in-house Microanalytical division of the Department.

General Procedure for the Preparation of 2-Naphthoxy Phenacyl Ketones **5-7**.

To a solution of dry acetone (20 ml) containing anhydrous K_2CO_3 (1.38 g, 10 mmol) was added 2-naphthol (0.576 g, 4.0 mmol) and appropriate phenacyl bromide (0.497 g, 2.5 mmol). The reaction mixture was gently reflux under N_2 atmosphere for 8-24 h. The reaction mixture was concentrated, diluted with water and extracted with CH_2Cl_2. The organic extract was washed repeatedly with 5% NaOH solution, then water and dried over anhydrous Na_2SO_4. Removal of solvent gave a crude solid which was purified by SiO_2 column chromatography to provide the desired product.

2-(Naphthalen-2-yloxy)-1-(4'-methoxyphenyl)-ethanone (**5**).

Following the general procedure, the reaction of 2'-bromo-4-methoxyacetophenone with 2-naphthol was carried out for 24 hr. The crude product was purified by SiO_2 column chromatography (elution with pet. ether:$CHCl_3$ 1:3) to provide **5** as a colourless solid, mp 85-87 °C in 60% yield. ^{1}H NMR ($CDCl_3$): δ 4.2 (3H, s, -OCH_3), 5.5 (2H, s, -CH_2), 7.0-8.3 (11H, m, ArH); IR (KBr, νmax/cm^{-1}): 3030, 1690, 1605, 1456, 1310, 1260. 1110, 945.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.08; H, 5.47. Found: C, 78.21; H, 5.47.

2-(Naphthalen-2-yloxy)-1-(4'-nitrophenyl)-ethanone (**6**).

Following the general procedure, the reaction of 2'-bromo-4-nitroacetophenone with 2-naphthol was carried out for 12 hr. The crude product was purified by SiO_2 column chromatography (elution with pet. ether:$CHCl_3$ 1:3) to provide compound **6** as a pale yellow solid, mp 148-149 °C in 30% yield. ^{1}H NMR ($CDCl_3$): δ 5.3 (2H, s, -CH_2), 7.0-8.35 (11H, m, ArH); IR (KBr, νmax/cm^{-1}): 3030, 1710, 1600,1520, 1425, 1340, 1210, 1085, 949.

Anal. Calcd. for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.23; N, 4.56. Found: C, 70.14; H, 4.49; N, 4.32.

2-(Naphthalen-2-yloxy)-1-(4'-pyridyl)-ethanone (**7**).

Following the general procedure, the reaction of 2'-bromo-4-acetylpyridine hydrobromide with 2-naphthol was carried out for 16 hr. The crude product was purified by SiO_2 column chromatography (elution with pet. ether:$CHCl_3$ 1:1) to provide compound **7** as a colourless solid, mp 136-138 °C in 29% yield. ^{1}H NMR ($CDCl_3$): δ 3.35 (2H, s, -CH_2), 7.0-8.65 (11H, m, ArH); IR (KBr, νmax/cm^{-1}): 3030, 1635, 1635,1500, 1455, 1338, 1230, 1066, 930.

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.56; H, 4.94; N, 5.32. Found: C, 77.44; H, 4.72; N, 5.12.

General Procedure for the Preparation of Naphthofurans **8-10**.

Appropriate naphthoxy-ketone (1 mmol) was dissolved in neat methanesulphonic acid (2.5 ml) and the reaction was allowed to proceed at room temperature overnight. The reaction mixture was diluted with cold water, neutralized with saturated Na_2CO_3 solution and extracted with CH_2Cl_2. The organic extract was washed repeatedly with water and dried over anhydrous Na_2SO_4. Removal of solvent gave a crude solid, which was purified by SiO_2 column chromatography to provide the desired naphthofuran.

11-(4'-Methoxyphenyl)naphtho[2,1-*b*]furan (**8**).

The cyclization of **5** using the general procedure gave up on work-up a crude solid which was purified by SiO_2 column chromatography (elution with pet. ether-$CHCl_3$, 1:4) to provide **8** as a colourless solid, mp 136-138 °C in 45% yield. ^{1}H NMR, see Table 1.IR (KBr, νmax/cm^{-1}): 3030, 2930, 1600, 1505, 1436, 1328, 1260, 1050, 945.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.21; H, 5.11. Found: C, 83.08; H, 5.38.

11-(4'-Nitrophenyl)naphtho[2,1-*b*]furan (**9**).

The cyclization of **6** using the general procedure gave up on work-up a crude solid which was purified by SiO_2 column chromatography (elution with pet. ether-$CHCl_3$, 1:4) to provide **9** as a pale yellow solid, mp 139-140 °C in 55% yield. ^{1}H NMR, see Table 1. IR (KBr, νmax/cm^{-1}): 3010, 2930, 1600, 1514, 1418, 1340, 1255 1040, 875.

Anal. Calcd. for $C_{18}H_{11}NO_3$: C, 74.74; H, 3.80; N, 4.84. Found: C, 74.42; H, 3.68; N, 4.63.

11-(4'-Pyridyl)naphtho[2,1-*b*]furan (**10**).

The cyclization of **7** using the general procedure gave up on work-up a crude solid which was purified by SiO_2 column chromatography (elution with pet. ether-$CHCl_3$, 1:2) to provide **10** as a pale yellow solid, mp 105-107 °C in 40% yield. ^{1}H NMR, see Table 1.IR (KBr, νmax/cm^{-1}): 3010, 1600, 1488, 1432, 1342, 1229, 10010, 1040, 940.

Anal. Calcd. for $C_{17}H_{11}NO$: C, 83.26; H, 4.48; N, 5.71. Found: C, 83.49; H, 4.31; N, 5.89.

11-(*N*-Methyl-4'-pyridinium)naphtho[2,1-*b*]furan Iodide (**11**).

Compound **10** (0.122 g, 0.5 mmol) was dissoved in dry THF (2 ml) and a few drops of CH_3I were added. The reaction flask was tightly stoppered and left at room temperature for a week to deposit crystals of **11**. The solvent was decanted out, crystals washed with little THF and dried under vacuum dessicator to give quantitative yield of **11** as a pale yellow crystalline solid, mp 242-243 °C. ^{1}H NMR, see Table 1.IR (KBr, νmax/cm^{-1}): 3010, 1630, 1560, 1430, 1344, 1270, 1120, 1040, 915, 875.

Anal. Calcd. for $C_{18}H_{14}NOI$: C, 55.81; H, 3.62; N, 3.62; I, 33.07. Found: C, 55.63; H, 3.76; N, 3.55; I, 32.77.

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[27] Electron density and geometry minimization were performed using Gaussian 98, Gaussian, Inc. Pittsburg, PA and calculations performed by Abinitio method at 6-31G (d) level.

[28] The X-ray crystal data have been submitted to the Cambridge database as a file CCDC-230654.