Research Article

Spectral analysis and crystal structure of two substituted spiro acenaphthene structures

J. Suresh[1], R.Vishnu Priya[1], S. Sivakumar[2] and R. Ranjith Kumar[2]

[1]Department of Physics, The Madura College (Autonomous), Madurai, 625 011, India
[2]Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai, 625 021, India

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Correspondence should be addressed to J. Suresh; Email: ambujasureshj@yahoo.com

Abstract

The crystal structure of spiro[2.2"]acenaphthene-1"-onespiro[3.3']-5'-(2-bromophenylmethylidene)-1'-methylpiperidin-4'-one-4-(2-bromophenyl) octahydroindolizine **(Ia)** and spiro[2.2"]acenaphthene-1"-onespiro[3.3']-5'-(4-bromophenylmethylidene)-1'-methylpiperidin-4'-one-4-(4-bromophenyl) octahydroindolizine **(Ib)** were elucidated by single crystal X ray diffraction. Compound (**Ia)**, $C_{37}H_{32}Br_2N_2O_2$, crystallizes in the Orthorombic system, space group $P2_12_12_1$ with a = 9.6989(5) Å, b = 16.3615(9) Å, c = 19.8997(11) Å and Z = 4. Compound **(Ib)**, having the same molecular formula, crystallizes in the monoclinic system, space group P 2_1/n with a = 8.3169(5) Å, b = 16.9397(9) Å, c= 22.2466 (13) Å, β = 96.943(3)° and Z = 4. The central piperidine ring adopts twisted conformation, the piperidine of octahydroindolizine ring is in half chair conformation and the pyrrole ring is in twisted envelope conformation in both the compounds **(Ia)** and (**Ib).** Details of the preparation, NMR and crystal structure determination and intra- and inter- molecular interactions of the compounds are given.

Introduction

Tuberculosis (TB) is an infectious disease caused by the bacterium Mycobacterium tuberculosis (MTB), which usually attacks the lungs but may also affect other parts of the body. This has been one of the most prevalent diseases responsible for the death of approximately one billion people during the last two centuries. TB remains a severe public health problem in India, accounting for nearly one-third of the global burden, and it has been estimated that 3.5 million people are infected with TB in that country alone (Granich *et al.* 2003) In the past years, only a few drugs have been approved by the Food and Drug Administration (FDA) to treat TB, which reflects the inherent difficulties in the discovery and clinical testing of new agents (O'Brien *et al.* 2001). Hence, the discovery of fast-acting new drugs to effectively combat TB is imperative.

In general, spiro compounds (Chande *et al.* 2005, Dandia *et al.* 2003) and nitrogen heterocycles (Sriram *et al.* 2006, Biava *et al.* 2006, Shaharyar *et al.* 2006) display good antimycobacterial activities. Recently, we reported an atom economic synthesis and evaluation of antimycobacterial activities of spiro pyrido-pyrrolizines and pyrrolidines, (Compounds 1–4) (Ranjith Kumar *et al.* 2008) which inhibited in vitro MTB and multi-drug resistant Mycobacterium tuberculosis (MDR-TB). In the course of screening to discover new compounds that could be useful for the treatment of TB, we herein report the synthesis, NMR spectra and single crystal X-ray studies of two novel spiro compounds, (**Ia)** and (**Ib)**. The chemical diagrams of the compounds (**Ia**) and (**Ib**) are shown in Figure 1.

In addition, it is also pertinent to note that the synthesis of biologically active indolizine derivatives continues to attract the attention of organic chemists, because of their wide spectrum of biological activity. Indolizine derivatives have been found to possess a

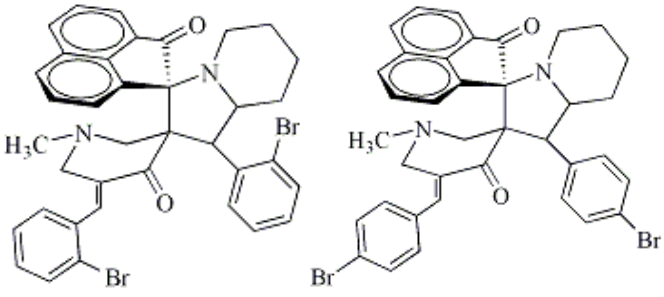

Figure 1. Chemical diagram of the molecule (**Ia**) (left) and (**Ib)** (right).

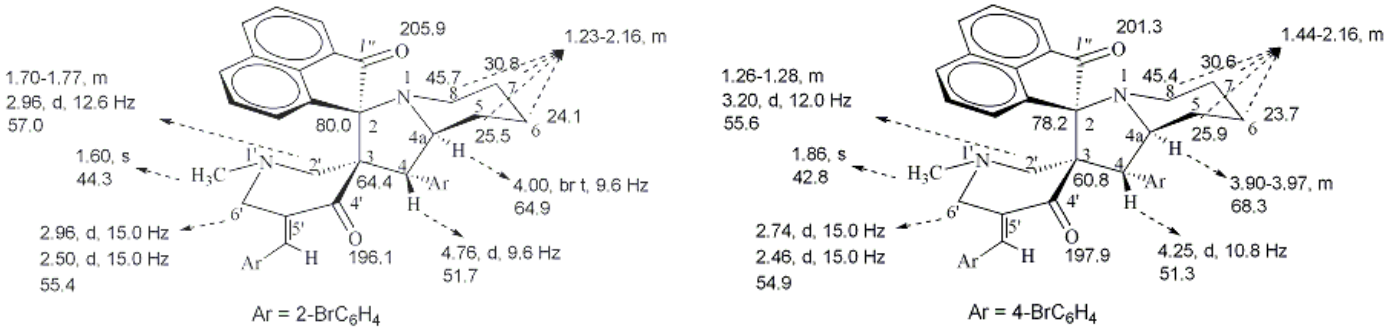

Figure 2. ^{1}H and ^{13}C NMR chemical shifts of **(Ia)** (left) and **(Ib)** (right).

variety of biological activities such as anti-inflammatory (Malonne *et al.* 1998), antiviral (Medda *et al.* 2003), aromatase inhibitory (Sonnet *et al.* 2000) as well as analgestic and antitumor (Pearson *et al.* 2001) ones. A brief survey of the Cambridge Structural Database (Version 5.33; Allen 2002) revealed a scarcity of precise crystallographic data on octahydroindolizine ring systems; hence, these structures are presumed to be very interesting and rarely studied moieties.

Experimental

Preparation of compound (Ia)

A mixture of 1-methyl-3,5-bis[(*E*)-2-bromo phenylmethylidene]tetrahydro-4(1*H*)-pyridinone (1 mmol), acenaphthenequinone (1 mmol) and piperidine-2-carboxylic acid (1 mmol) was dissolved in isopropyl alcohol (15 mL) and heated to reflux for 60 min. After completion of the reaction as evident from TLC, the mixture was poured into water (50 mL), the precipitated solid was filtered and washed with water (100 mL) to obtain pure yellow solid having a melting point of 226°C (Yield : 95%).

Preparation of compound (Ib)

A mixture of 1-methyl-3,5-bis[(*E*)-4-bromo phenylmethylidene]tetrahydro-4(1*H*)-pyridinone (1 mmol), acenaphthenequinone (1 mmol) and piperidine-2-carboxylic acid (1 mmol) was dissolved in isopropyl

Table 1. The crystal data, experimental conditions and structure refinement parameters of the compound **(Ia)** and **(Ib)**.

Empirical formula	**$C_{37}H_{32}Br_2N_2O_2$**	**$C_{37}H_{32}Br_2N_2O_2$**
Formula weight	696.47	696.47
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	$P2_12_12_1$, orthorhombic	P 2_1/n, monoclinic
Unit cell dimensions	a = 9.6989(5)Å b=16.3615(9)Å c = 19.8997(11)Å	a = 8.3169(5)Å, b =16.9397(9) Å, c = 16.9397(9)Å,β=96.943(3)°
Volume	3157.85 (3) $Å^3$	3111.2(3) A^3
Z, Calculated density	4, 1.46mg/m^3	4, 1.487 mg/m^3
Absorption coefficient	2.603 mm^{-1}	2.642 mm^{-1}
F(000)	1416	1416
Crystal size	0.19x0.16x0.14mm^3	0.17x0.14x0.11mm^3
Theta range for data collection	1.6 to 28.3deg	1.52 to 28.44 deg
Limiting indices	-12<=h<=12,-11,=k<=20 -25<=l<=26	-10<=h<11,-22<=k<21, -29<=l<=29
Reflections collected / unique	17252 / 7629 [R(int) = 0.0288]	29716 / 7760[R_{int} = 0.0649]
Completeness to theta	98.3 %	98.9%
Absorption correction	ω –scan	ω –scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7629 / 0 / 389	7760/ 0/ 389
Goodness-of-fit on F^2	1.006	1.006
Final R indices [I>2sigma(I)]	R_1 = 0.0394, wR_2 = 0.0701	R_1 = 0.0510, wR_2 = 0.1034
R indices (all data)	R_1 = 0.0803, wR_2 = 0.0778	R_1 = 0.1131, wR_2 = 0.1220
Largest diff. peak and hole	0.517 and -0.549 eA^{-3}	0.406 and -0.606 $eÅ^{-3}$

alcohol (15 mL) and heated to reflux for 60 min. After completion of the reaction as evident from TLC, the mixture was poured into water (50 mL), the precipitated solid was filtered and washed with water (100 mL) to obtain pure yellow solid having a melting point of 226°C (Yield : 95%)

Structure Determination and Refinement

Single crystal X-ray intensity data of compound **(Ia)** and compound **(Ib)** were collected using Bruker SMART APEX2 CCD diffractometer with MoKα radiation (λ=0.71073Å) at room temperature (293 K). The data reduction was performed with SAINT (Bruker, 2004). An absorption correction was made using the ω-scan method. The structures of both compounds were solved using the direct methods SHELXS97 (Sheldrick 2008) and all the non-hydrogen atoms were refined anisotropically by full matrix least-squares based on the F^2 of all unique reflections using SHELXL97 (Sheldrick 2008). Molecular graphics were drawn using PLATON (Spek 2009). The hydrogen atoms were placed in calculated positions and included in the refinement using the riding model with C—H = 0.93–0.98 Å and U_{iso} = 1.2*U*eq(C,) for the CH, CH_2 groups and U_{iso} = 1.5*U*eq(C) for the CH_3 group. The crystal data, experimental conditions and structure refinement parameters for the compounds **(Ia)** and **(Ib)** are presented in Table 1.

Results and Discussion

Spectral Data

The structure of the compounds (**Ia)** and (**Ib)** has been elucidated using ^{1}H, ^{13}C and two dimensional NMR spectroscopic studies. The ^{1}H and ^{13}C NMR chemical shifts of (**Ia)** and (**Ib)** are shown in Figure 2.

It is interesting to observe that the chemical shifts of 2′-CH_2 of (**Ia)** (2.96 ppm and ~1.70 ppm) and

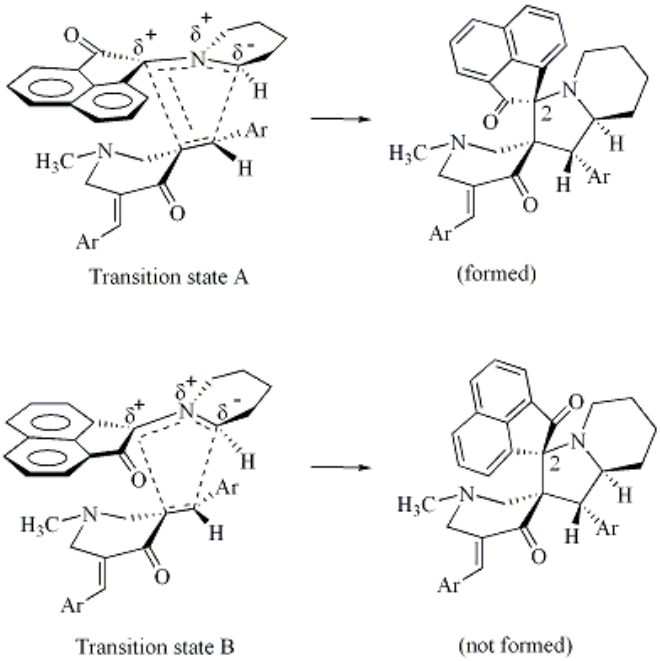

Figure 3. Stereochemistry of formation of cycloadducts differing in their configurations at C-2.

(**Ib)** (3.20 ppm ~1.27 ppm) differ greatly by 1.26 and 1.93 ppm, respectively. This suggests that probably the H-2eq is spatially proximate to the carbonyl of acenaphthylen-1(2*H*)-one, shifting it downfield, while H-2ax lies in the shielding zone of the acenaphthylen-1(2*H*)-one ring, shifting it downfield, suggesting relative configuration at C-2 for (**Ia)** and (**Ib)**. The alternative stereochemistry with inversion of the configuration at C-2 relative to that shown on (**Ia)** or (**Ib)**, bringing both the carbonyls of the piperidone and acenapthene rings towards each other in spatial proximity, probably renders the transition state of the cycloaddition unstable by electrostatic repulsion, which could raise the free energy of activation (transition state B in Figure 3) relative to the transition state leading to the

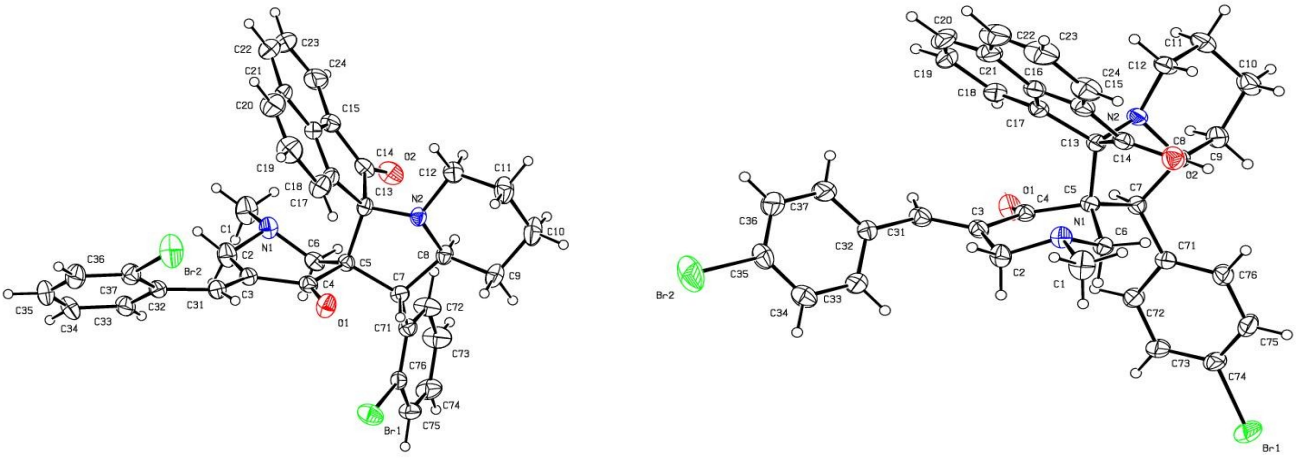

Figure 4. The molecular structure of compound **(Ia)** (left) and **(Ib)** (right) showing the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level, using ORTEP 3. Hydrogen atoms are drawn as spheres of arbitrary size.

formation of (**Ia)** or (**Ib)** with both carbonyls placed far off (transition state A in Figure 3).

The biological activity studies of the compounds (**Ia)** and (**Ib)** are presently in progress. Apart from screening these compounds against MTB, their activity against Alzheimer's disease and cancer is also being examined.

Crystal structure

Figure 4 shows the ORTEP plot, drawn at 30 % probability displacement ellipsoids of compound (**Ia**) and (**Ib**) and the atom-numbering scheme. The six membered piperidine rings in the title compounds adopt twisted half chair conformation as evident from puckering parameters Q = 0.567(3) Å, θ = 134.8(3)° and Φ = 140.3(5)° in compound **(Ia)** and Q = 0.554(3) Å, θ = 33.1(3)° and Φ = 316.6(5)° in compound **(Ib)** (Cremer & Pople 1975). The differences in the deviations are due to steric hinderance of the different substituents at the C3 and C5 positions of the piperidine ring. The olefinic double bond in the structures has an E configuration. From the puckering parameters, Q = 0.393(3) Å and Φ = 10.3(5)° in compound **(Ia)** as well as Q = 0.439(3) Å and Φ = 207.7(4) in compound **(Ib)** (Cremer & Pople 1975), the pyrrole ring is shown to be in a twisted envelope conformation.

The piperidine of octahydroindolizine ring is in half chair conformation as their puckering parameters are Q = 0.573(4) Å, θ = 177.9(4)° and Φ = 220(9)° in compound **(Ia)** and Q = 0.568(3) Å, θ = 0.0(3)° and Φ = 127(14)° in compound **(Ib)** (Cremer & Pople 1975). The dihedral angles between the piperidone mean plane and the aryl rings are 45.29(1)° , 84.01(1)° in (**Ia**) and 66.23 (1)°, 87.03 (1)° in (**Ib**), respectively. As a result, the torsion angle C3-C31-C32-C33 has the value 41.50(3)° in (**Ia**) and -51.55(3)° in (**Ib**). This lack of coplanarity is caused by nonbonded interactions between one of the ortho H atoms in the aryl ring and the equatorial H atoms at the 2-position of the piperidone ring (H33/H2A or H2B). As a result of these steric repulsions the bond angle C3-C31-C32 is expanded in both compounds, being 128.75 (19)° in

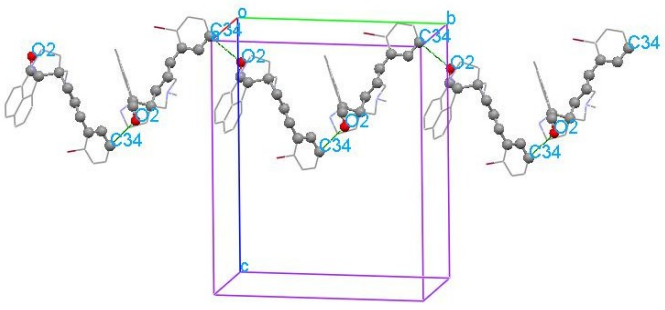

Figure 5. Linear zigzag chain motif $C_1^1(11)$ of compound **(Ia)**.

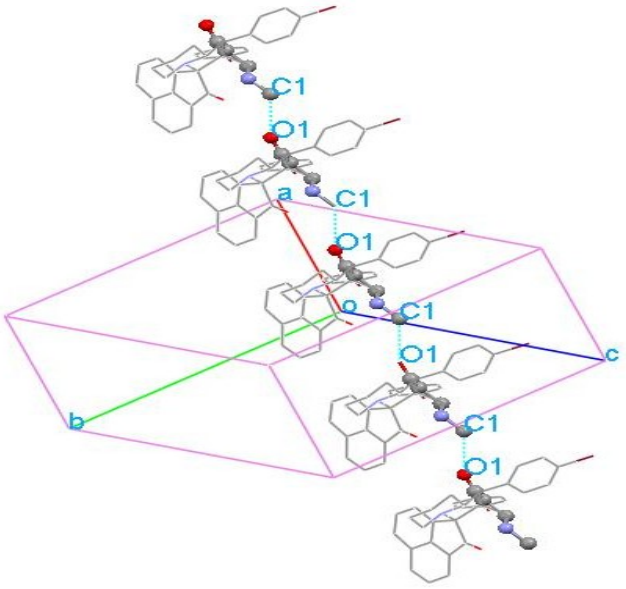

Figure 6. Linear chain motif $C_1^1(7)$ of compound **(Ib)**.

(**Ia**) and 127.48(18)° in (**Ib**), instead of 120°. The bromophenyl rings are planar, as confirmed by the values of the r.m.s. deviation; 0.0038 and 0.0163Å in compound (**Ia**), 0.0118 and 0.0122 in compound (**Ib**). The dihedral angle between the bromophenyl rings is 72.2 (1)° and 63.09(1)° in (**Ia**) and (**Ib**), respectively. These rings are making angles of 35.4 (1)° and 74.3 (1)° in (**Ia**), 41.89(1)° and 79.92(1)° in (**Ib**), with their respective acenaphthene group.

The C_{sp}^2 to C_{sp}^2 distances in the acenaphthene group ranges from 1.335 (3) (C19-C20) to 1.570 (2) Å (C13-C14) in (**Ia**), 1.400 (3) (C19-C20) to 1.572(2) Å (C13-C14) in (**Ib**) and the C-C-C bond angles ranges from 101.02 (16)° in (**Ia**), 101.94(16)° in (**Ib**) (C14-C13-C17) to 123.58 (2)° in (**Ia**) and 122.71(2)° in (**Ib**) (C15-C16-C21). These values are in agreement with previously reported values of related structures (Hazell et al, 1976; Hazell et al, 1977; Jones et al, 1992; Sundar et al, 2002). The C8-N2 bond distance, being 1.454Å (3) ° in (**Ia**) and 1.461Å (3) ° in (**Ib**) is comparable to the C_{sp}^2-N_{sp}^2 distances found in similar structures (Sussman *et al.* 1973, Wodak *et al.* 1975). In both crystal structures weak C—H···O interactions have been observed (see Table 2 and 3).

Crystal Packing

In the crystal structure of the compound (**Ia)** the adjacent molecules are connected via a C34—H34···O2 interaction, leading to a chain $C_1^1(11)$ motif (Bernstein et al, 1995) around the inversion centers of the unit cell. These motifs form a linear infinite chain running along the a-axis, as shown in Figure 5. In the crystal structure of the compound (**Ib)** the adjacent molecules

are connected via a C1—H1C···O1 interaction, leading to a chain $C_1^1(7)$ motif (Bernstein *et al.* 1995) around the inversion centers of the unit cell. These motifs form a linear infinite chain running along the b-axis as shown in Figure 6. Neither C-H…O nor C-H…π interactions are observed between these chains. However there are several van der Walls interactions between them in both compounds. Inter molecular and intra molecular hydrogen bond geometry of molecules (**Ia)** and (**Ib)** are listed in Tables 2 and 3, respectively.

Table 2. Hydrogen bonds [Å and °] of compound **(Ia)**.*

D-H...A	d(D-H)	d(H...A)	d(D...A)	DHA
C(6)-H(6A)...O(2)	0.97	2.38	2.998(4)	121
C(7)-H(7)...Br(1)	0.98	2.67	3.213(3)	115
C(8)-H(8)...O(2)	0.98	2.55	3.143(4)	119
C(18)-H(18)...O(1)	0.93	2.59	3.178(4)	122
C(34)-H(34)...O(2)^{i}	0.93	2.51	3.272(5)	140

*The symmetry transformations used to generate equivalent atoms are the following:
(i) 1- x, ½+y, ½- z

Table 3. Hydrogen bonds [Å and °] of compound **(Ib)**.*

D-H...A	d(D-H)	d(H...A)	d(D...A)	DHA
C(6)-H(6B)...O(2)	0.97	2.36	2.928(3)	117
C(1)-H(1C)...O(1)^{i}	0.96	2.59	3.456(4)	151

*The symmetry transformations used to generate equivalent atoms are the following:
(i) -1+x,y,z

Conclusion

Spiro[2.2"]acenaphthene-1"-onespiro[3.3']-5'-(2-bromophenylmethylidene)-1'-methylpiperidin-4'-one-4-(2-bromophenyl)octahydroindolizine **(Ia)** and spiro [2.2"]acenaphthene-1"-onespiro[3.3']-5'-(4-bromophenylmethylidene)-1'-methylpiperidin-4'-one-4-(4-bromophenyl) octahydroindolizine **(Ib)** were synthesized. The single crystals of compounds (**Ia**) and (**Ib)** were obtained by the slow evaporation method (solvent: 1:1 ethyl acetate-ethanol). The conformational features of the compounds (**Ia**) and (**Ib)** in the solid and liquid phase are discussed, using X-ray and NMR methods, respectively. The bond angles C3-C31-C32 and C8-C7-C71 presented here and the values found in similar structures (Suresh *et al.* 2012) are useful in the design of additional analogues. The replacement of the equatorial H atoms at the 2- and 6-positions, and the inclusion of substituents of varying sizes at atoms C33, C37, C72 and C76, are likely to alter the C3-C31-C32 and C8-C7-C71 bond angles. Correlations have been established between the bond angle values and bioactivity (Pandeya & Dimmock 1977). In addition, the increased ψ values would lead to variations in the relative locations of the aryl rings, which could affect the alignment of these rings at a binding site and hence influence bioactivity (Quail *et al.* 2005). Further studies on structure-bio activity relationships of these compounds are in progress in our research group.

Supplementary Material

Crystallogtaphic data (excluding structure factors) for the structures of **(Ia)** and **(Ib)** reported in this paper have been deposited with the Cambridge Crystallographic data Centre as supplementary publication CCDC 892957 & CCDC 892958. Copies of the data can be obtained, free of charge, on application to, CCDC, 12 Union Road, Cambridge, and CB2 1 EZ UK; Fax: 044-1223-336033; Email: deposit@ccdc.cam.uk or at: http://www.ccdc.cam.ac.uk/.

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Conflicts of Interest

The authors declare no conflicts of interest.

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