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Coordination of bromide anions and organic bromine to tryptophan ligands

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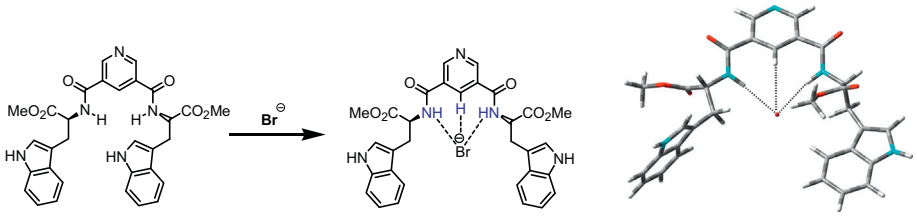
GRAPHICAL ABSTRACT

Two tryptophan-based pyridine dicarboxamide ligands have been synthesised and characterized. ^{1}H NMR studies indicated that these ligands are capable of coordinating to bromide anions through amide/indole NH and CH groups. Based on ^{1}H NMR studies, we found that organic bromides selectively bind to with one of the ligands, as evidenced by complexation induced chemical shifts for the indole and amide NH resonances.



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ABSTRACT

Two tryptophan-based pyridine dicarboxamide ligands have been synthesised and characterised. 1H NMR studies indicated that these ligands are capable of coordinating to bromide anions through amide/indole NH and CH groups. Based on 1H NMR studies, we found that organic bromides selectively bind to with one of the ligands, as evidenced by complexation induced chemical shifts for the indole and amide NH resonances.

1. Introduction

Recent studies have established that tryptophan plays critical role in biomolecular systems by stabilizing aromatic interactions [1–4] and facilitating cation–π interactions [3,5]. Such interactions have immense significance in biology, especially in context of molecular recognition [6]. Again, it has been found that tryptophan residues can participate in halide binding, as elucidated in the crystal structure of *haloalkane dehalogenase* [7–9]. This has, in fact, attracted immense interest and several groups have explored the indole motif [10–11] and bis-indole derivatives [12–14] as potential receptors for anions. During the course of these investigations, important aspects related to the nature of interactions between indole-based host molecules with various anions have been unraveled. An early example was reported by Gale and co-workers [15] who found that indole-based pyridine-2,6-dicarboxamide and isophthalamide clefts exhibits strong affinity for fluoride in dimethyl sulfoxide/water mixtures, compared to other halides. Subsequent studies involving functionalized indole derivatives [12–16] have led to the development of receptors for various anions such as fluoride, chloride, acetate and phosphate. In addition,

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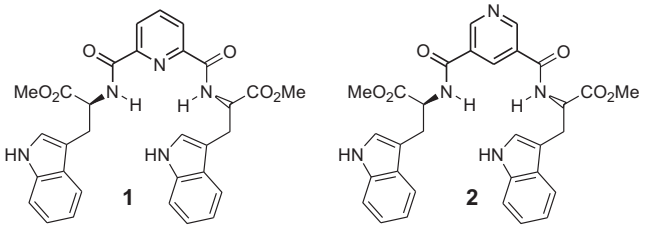
studies in the field of anion coordination have established the pyrrole [16–17] and pyridine derivatives [18–20] as useful motifs for the coordination and binding of anions. However, in this backdrop, several crucial aspects related to the coordination ability of tryptophan towards bromide anions, and in particular organic bromide remain relatively unknown [14].



Herein we report the synthesis and characterization of tryptophan-based ligands **1** and **2**, and delineate their coordination ability towards bromide anions vis-à-vis organic bromine using ^{1}H NMR spectroscopy.

2. Experimental section

All chemicals were commercially available from Sigma–Aldrich or Merck or Spectrochem (India) and used as received. Solvents for spectroscopic and fluorescence experiments were distilled under nitrogen atmosphere before use. All ^{1}H and ^{13}C NMR were recorded on a Bruker 300 MHz spectrometer, and all experiments were performed at 298 ± 1 K; the chemical shifts are reported in parts per million (ppm), and calibrated to the residual solvent peak. The electronic absorption spectra were recorded on a Shimadzu UV–VIS spectrophotometer. Fluorescence spectra for the compounds were recorded on a Hitachi steady-state fluorimeter, and all experiments were performed using solvents distilled under nitrogen atmosphere.

2.1. Synthesis of ligands *1* and *2*

In a typical experiment, L-tryptophan methyl ester hydrochloride (0.510 g, 2 mmol) was dissolved in dichloromethane (20 mL) under nitrogen atmosphere. The solution was cooled to 0 °C (using ice-bath), and pyridine-2,6-dicarbonyl chloride (0.202 g, 1 mmol) was added followed by Et_3N (0.7 mL, 5 mmol) and DMAP (catalytic amount). This reaction mixture was stirred overnight under N_2. After completion, the reaction mixture was diluted with dichloromethane and extracted successively with water, sodium bicarbonate solution (10% aqueous) and distilled water. Finally the organic extracts were collected and dried over anhydrous Na_2SO_4. The crude product was purified by flash column chromatography (dichloromethane–hexane as eluent) which gave ligand **1** as pale yellow solid; Yield 64%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (bs, 2H, NH), 8.36 (d, 2H, ArH, J = 7.8 Hz), 8.09 (m, 3H, ArH), 7.51 (d, 2H, NH, J = 4.8 Hz), 7.11 (m, 4H, ArH), 7.01 (s, 2H, ArH), 6.65 (s, 2H, CH), 5.22 (q, 2H, CH, J = 2.6 Hz), 3.85 (s, 6H, OMe), 3.42–3.32 (dd, 2H, CH2, J = 4.8 Hz, 4.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.1, 162.8, 148.5, 139.1, 135.9, 126.8, 125.5, 123.3, 122.1, 118.0, 111.8, 108.4, 77.4, 76.5, 52.7, 51.6, 28.0.

Ligand **2**: Prepared following the same procedure given above using pyridine-3,5-dicarbonyl dichloride and tryptophan methyl ester hydrochloride as starting materials. The desired ligand **2** was obtained as a pale yellow solid after column purification. Yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$): 8.78 (s, 2H, NH), 8.43 (s, 2H, ArH), 8.08 (s, 1H, ArH), 7.47 (d, 2H, NH, J = 8 Hz), 7.25 (s, 1H, ArH), 7.10–7.01 (m, 7H, ArH), 6.85 (s, 2H, ArH), 5.08 (q, 2H, CH, J = 6 Hz), 3.45 (s, 6H), 3.40–3.20 (dd, 4H, CH_2, J = 6 Hz, 6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 164.5, 150.7, 136.0, 133.3, 128.9, 127.2, 123.0, 122.3, 119.6, 118.3, 111.5, 109.5, 76.5, 53.3, 52.6, 27.3.

2.2. NMR experiments: Calculation of association constants (Ka)

All the ^{1}H NMR experiments of ligands **1** and **2** (2 mg in 0.5 mL) with bromide anions were performed in CD_3CN, with ligand concentration constant. The experiments involving organic bromides and ligands **1** and **2** (2 mg in 0.5 mL) were performed in $CDCl_3$ at 298 ± 1 K. Stock solutions of the bromide salt/organic bromides (concentration = 60 mM) were prepared in $CDCl_3$ or CD_3CN, and added in aliquots of 5 μL.

In each case, the *Ka* values were obtained from the titration of ligands **1** and **2** with the tetramethyl ammonium bromide salts (TMAB) and organic bromides. Changes observed in the amide NH resonance $1/(\delta_o - \delta_{obs})$ were plotted as function of reciprocal of guest concentration [*S*], and the values of association constants (*Ka*) were calculated according to Benesi–Hildebrand method [21]. Here, δ_o corresponds to the chemical shift of the free ligand (for **1** or **2**), δ_{obs} is the observed complexation induced chemical shift in the presence of various guest (TMAB or organic bromides). The linear relationship between $1/(\delta_o - \delta_{obs})$ and the reciprocal of the guest concentration indicates the formation of a 1:1 complex between guest and the receptor.

3. Results and discussion

3.1. Synthesis of ligands, UV–visible and fluorescence characterization

Ligands **1** and **2** were synthesized by coupling pyridine-2,6-dicarbonyl chloride and pyridine-3,5-dicarbonyl chloride respectively with tryptophan methyl ester hydrochloride. These ligands were characterized using UV–visible, fluorescence spectroscopy, and NMR spectroscopy. As shown in Fig. 1, the absorption spectra of **1** and **2** recorded in acetonitrile exhibited similar absorptions at λ_{max} 286 nm as expected for Trp-derivatives [22]. Steady-state fluorescence experiments indicated that when irradiated at 300 nm in acetonitrile [23], compound **1** exhibited two emissions at 373 and 455 nm, while **2** fluoresced at 434 nm (λ_{em}); the emission quantum yields were found to be 0.14 for **1** and 0.05 for **2** with reference to tryptophan [24]. We suggest that, of the two emissions at 373 and 455 nm observed for **1**, the latter could originate from excimer fluorescence of tryptophan [25].

3.2. NMR studies of *1* and *2* with bromide anion and organic bromides

In our next experiment, we performed ^{1}H NMR investigations on ligands **1** (and **2**) in the presence of added bromide anion (i.e. TMAB) so as to rationalize the anion coordination ability of the amide/indole NH groups.

Accordingly, we added bromide ions to ligand **1** in CD_3CN (acetonitrile-d^3) and monitored the chemical shift changes for the indole and amide NH resonances using ^{1}H NMR. As shown in Fig. 2, the addition of bromide to **1** caused the indole NH resonances (of **1**) to shift downfield from 9.10 to 9.21 ppm, while the amide NH resonances were shifted by $\Delta\delta \sim 0.1$ ppm (in the presence of excess TMAB). We propose that **1** could adopt intramolecularly N–H···N hydrogen bonded cleft-like structure [26] such as **1-Br** (Scheme 1), wherein the bromide anion can be stabilized by coordination to the indole and amide NH groups. The spectral changes observed for the indole NH resonances upon addition of bromide anion were analyzed according to Benesi–Hilderbrand method, which gave *Ka* = 45 ± 4 M^{-1}, indicative of weak binding

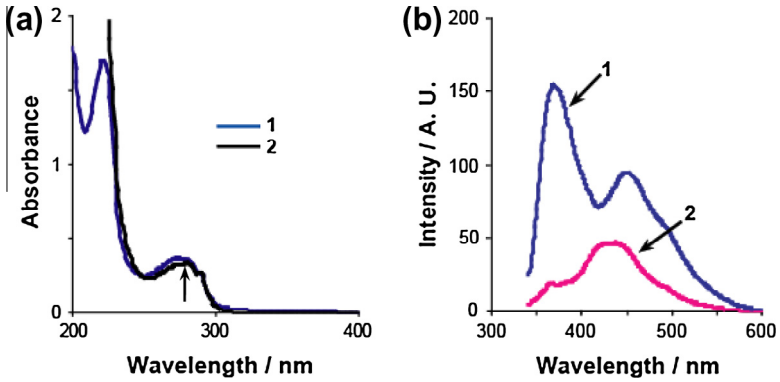


Fig. 1. (a) UV–visible spectra of **1** and **2** in acetonitrile (conc. 4.0×10^{-4} M; arrow indicate λ_{max} 285 nm); (b) fluorescence spectra of **1** (emission maxima, 373 and 455 nm) and **2** (emission maxima, 434 nm) in acetonitrile (conc. 4.0×10^{-5} M; λ_{ex} at 300 nm).

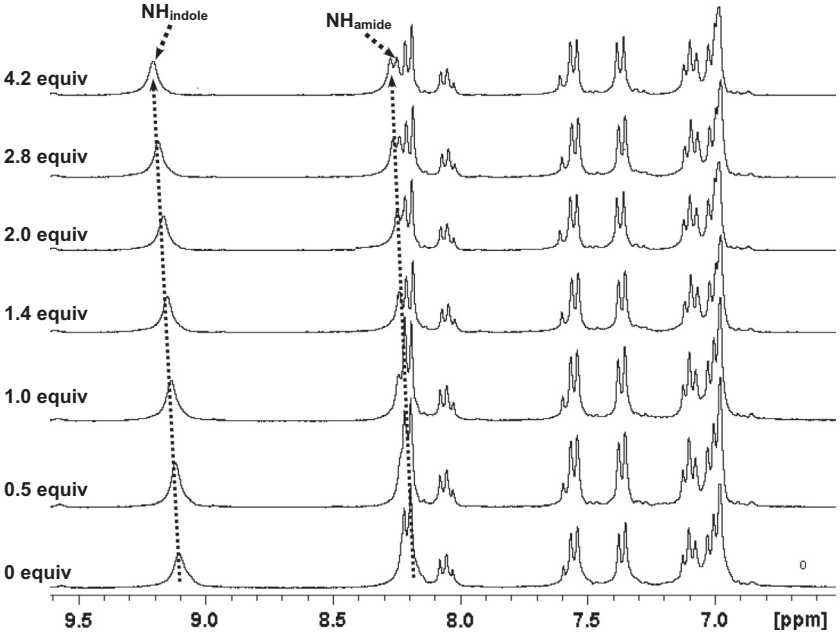
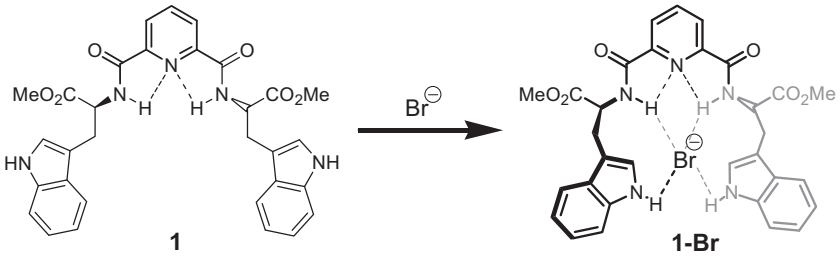


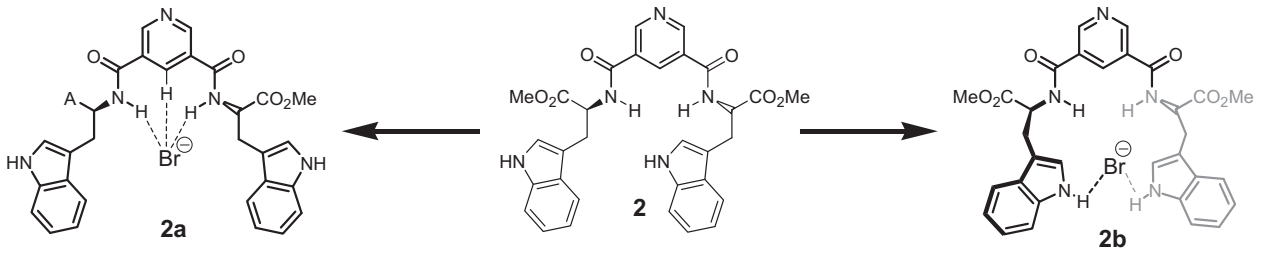
Fig. 2. Partial ^{1}H NMR spectra in CD_3CN depicting the changes in chemical shifts of indole and amide NH resonances of **1** (0.007 M) at different concentrations of TMAB ($Ka = 45 \pm 4\ M^{-1}$).



Scheme 1. Intramolecular hydrogen bonding interactions in **1** and bromide anion.

in **1**-**Br** complex. Notably, analogous 2,6-dicarboxamides derivatives have been described wherein the indole pendant groups can be pre-organized through intra-molecular hydrogen bonding to produce a cleft-like structure [15]; it was reported that this ligand was suitable for binding fluoride and chloride anions in dimethyl sulfoxide/water, whereas the bromide anion did not interact.

In order to compare the possible role of intra-molecular hydrogen bonds, we examined the effect of bromide anion coordination on ligand **2** with regard to the indole NH and amide NH groups. As illustrated in Scheme 2, the coordination of bromide anion to ligand **2** would produce either structure **2a** or **2b**, which can be identified based on the complexation-induced chemical shift changes for the amide NH vis-à-vis indole NH resonances. Accordingly we



Scheme 2. Possible coordination modes of **2** with the bromide anion.

performed ^{1}H NMR titrations of **2** with TMAB in order to identify the nature of interactions between the ligand and the bromide anion.

As monitored by ^{1}H NMR, the addition of TMAB to **2** in CD_3CN caused the pyridine CH (of **2**) and the amide NH resonances to shift downfield (Fig. 3a); the *pyridine CH and amide NH resonances shifted from 8.30 to 8.68 ($\Delta\delta$ = 0.38 ppm), and 7.53 to 8.06 ppm ($\Delta\delta$ = 0.53 ppm) respectively* while the indole NH shifted upfield (9.24 ppm at 0.5 equiv TMAB) and then slightly downfield to 9.33 ppm. As shown in Fig. 3b, the larger complexation induced chemical shifts were noted for the amide NH resonances, indicative of N–H···Br$^-$ interactions. In comparison, the role of the indole NH groups in bromide coordination was less significant ($\Delta\delta$ < 0.1 ppm), unlike in the case of ligand **1**. As depicted in Fig. 3c, distinct complexation induced shifts observed for pyridine CH groups of **2** indicating the presence of C–H···Br$^-$ interactions; these C–H···Br$^-$ interactions contribute to the binding of the bromide anions, and emanated from concomitant formation of N–H···Br$^-$ hydrogen bonds.

In fact, aromatic CH groups have been known to contribute to anion coordination and the effects most prominent cationic host molecules; for instance, prominent CH···anion interactions have been recognized with fluoride or chloride anions binding in imidazolium and pyridium hosts [27]. Additionally, the resonance signals due to the methylene protons of **2** (cf. the indole ring) emerged as a doublet (see Fig. S7, Supplementary Materials); this observation points to proximal interactions of the bromide anion to the methylene protons. Following this, we analyzed the stoichiometry of the bromide complex of **2** using Job's method [21,28] which indicated the formation of 1:1 complex, with *Ka* = 150 ± 12/M.

In the absence of crystallographic evidence, we attempted modeling the structures of ligands **1** and **2** using DFT calculations

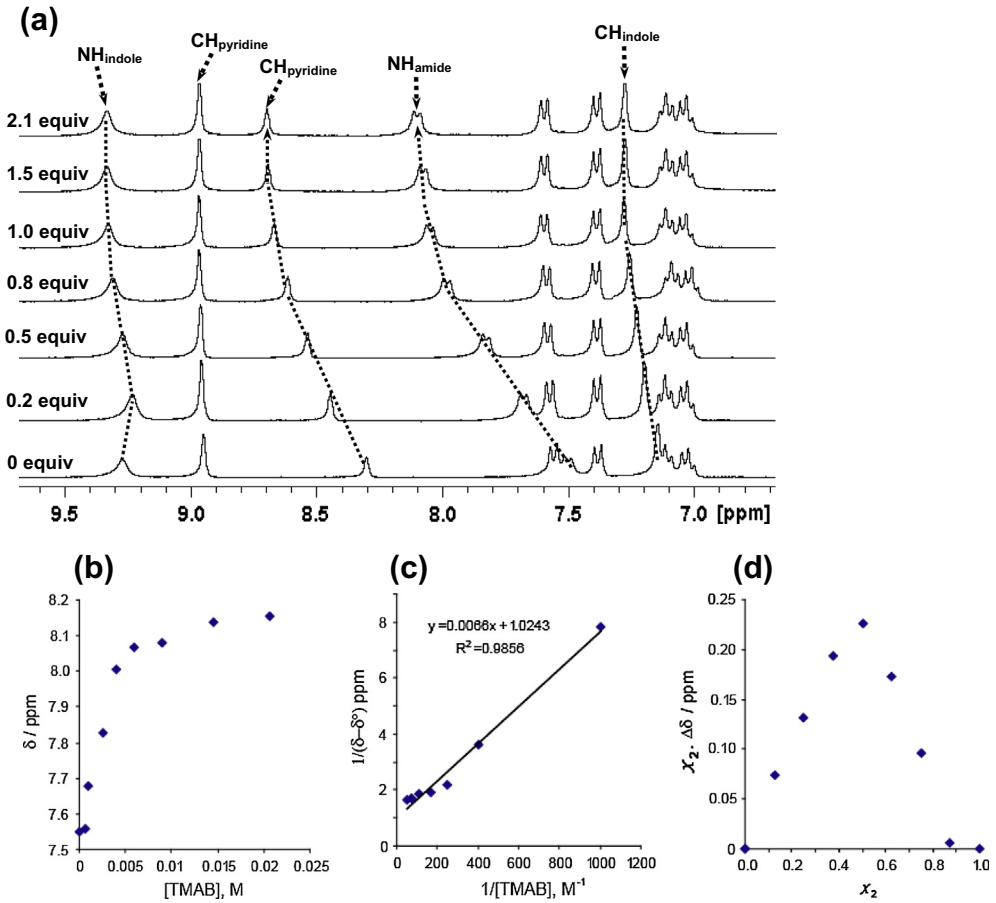


Fig. 3. Interaction of ligand **2** (0.007 M) with bromide anion: (a) Partial ^{1}H NMR spectra in CD_3CN indicating chemical shift changes in **2** following addition of bromide (as TMAB). (b and c) Plots showing chemical shift changes of amide NH resonances upon addition of bromide anion, and the corresponding Benesi–Hilderbrand analysis (*Ka* = 150 ± 10 M^{-1}). (d) Job's plot for **2**-Br complex, where X_2 = mole fraction of **2**, $\Delta\delta$ = complexation induced chemical shifts for **2**-**Br**.

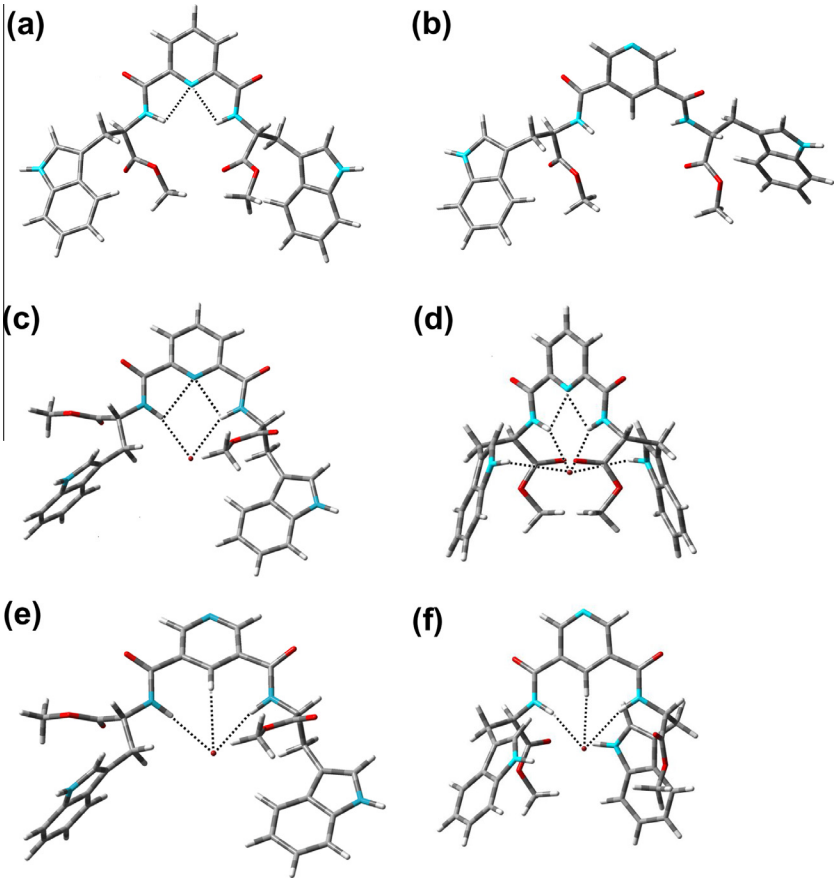


Fig. 4. Optimized structures for: (a) **1** (intramolecular N–H···N: 2.27 Å, 105° and 2.30 Å, 104°); (b) **2**; (c) **1** with bromide, without coordination of indole NH group (intramolecular N–H···N: 2.47 Å, ~96° and 2.34 Å, 101°; 2.56 Å, 153° and 2.47 Å, 162°); (d) **1** with bromide, invoking indole NH group (intramolecular N–H···N: 2.33 Å, 101°; amide N–H···Br^-: 2.48 Å, ~90° and 2.47 Å, 96°; indole N–H···Br^-: 3.49 Å, ~169°); (e and f) **2** with bromide, with two possible orientations indole group. Calculations favor formation of the former structure which invokes with N–H···Br^- (2.43 Å, 169° and 2.44 Å, 172°) and C–H···Br^- (2.94 Å, 119°) interactions.

(Fig. 4). The geometrical minima of the ligand species with and without bromide anions were optimized at B3LYP/6-31+G(d) level of theory using Gaussian 09 [29]. The optimized structure of ligand **1** (Fig. 4a) indicated intramolecular hydrogen bonds involving the amide NH groups as donors and the pyridine N as acceptor whereas such interactions were absent in ligand **2** (Fig. 4b). Fig. 4c and d shows two possible structures for **1** in the presence the bromide anion, which could be produced depending on the orientation of the indole rings; the calculations indicated that the structure shown in Fig. 4d to be favored (~4.89 kcal/mol over Fig. 4c), in which the bromide coordinated to both the amide NH and indole NH groups. The structure shown in Fig. 4d indicate N–H···Br^- hydrogen bonds for the amide NH group [2.48 Å, ~90° and 2.47 Å, 96°], while it was found to be 3.49 Å (~169°) for the indole NH groups. This was in agreement with the ^{1}H NMR analysis, that the interactions of bromide with **1** invoking the indole and amide NH groups were relatively weak. In comparison, the structure shown in Fig. 4c indicated N–H···Br^- hydrogen bond involving the amide NH with parameters 2.56 Å (153°) and 2.47 Å (162°), while the indole NH group did not participate.

As shown in Fig. 4e, the complex of ligand **2** with bromide anion exhibited strong N–H···Br^- interactions, wherein the bond parameters were 2.43 Å (169°) and 2.44 Å (172°). In this situation, the bromide anion preferentially coordinated to the amide NH groups with additional C–H···Br^- interactions. In fact, the optimized structures indicated C–H···Br^- interactions for the pyridine CH with bond parameters of 2.94 Å (119°), while for methylene CH groups the distances were found to be 2.89 Å (154°) and 3.03 Å (123°) respectively. The possibility of indole adopting a different orientation was also explored (Fig. 4f; 2.41 Å, 119°; 2.49 Å, 119°) which was found to be disfavored by 3.02 kcal/mol compared to the structure illustrated in Fig. 4e. Moreover, the structure shown in Fig. 4e reveals stabilizing C–H···Br^- interactions invoking the methylene groups which was in accordance with the ^{1}H NMR observations. Based on these parameters, it seems that both ligands **1** and **2** coordinate to the bromide anion, although the latter was apparently more effective given the larger complexation induced ^{1}H NMR shifts.

Having unraveled the bromide anion binding ability of the tryptophan-based ligands, we were intrigued by the question whether ligands **1** and **2** could coordinate of neutral organic bromides. The possible coordination of an organic halide to tryptophan and the role of hydrogen bonding in the binding process is important area of research [8]. The elucidation of such interactions would be relevant considering its implications in the biology and environment [8,30], such as the bioremediation of potentially toxic halogen-based compounds. In this light, we studied the interactions of ligands **1** and **2** towards selected organic bromides, viz., bromobutane, benzyl bromide and bromobenzene, in order to delineate the efficacy of indole/amide NH groups in the coordination of neutral molecules.

In this context, we studied mixtures of **1** and bromobutane-1, benzyl bromide and bromobenzene respectively in $CDCl_3$ using ^{1}H NMR so as to explore the possible complexation of organic bromides. However, ligand **1** was not effective in coordinating to organic bromides as the addition of organic bromides did not result

in perceptible chemical shifts changes to the indole/amide NH resonances (Fig. S8).

Interestingly, the addition of bromobutane-1 (1.0 equiv) to solution of **2** in $CDCl_3$ revealed distinct downfield shift of the indole NH resonances (8.854–8.873 ppm, Fig. 5), while the amide NH resonances were shifted upfield (from 6.931 to 6.89 ppm, obscured by the aromatic signals). The resonances for CH protons sandwiched between the two amide NH groups for **2** also exhibited minor upfield shift, apparently reflecting the increase in electron density due to coordination of the organic bromide. The complexation induced chemical shifts observed in this case were different from those for **2**-Br^- system which were reasonable because the coordination of organic bromide to **2** involves a neutral molecule, rather than bromide anion.

Subsequently we investigated the mixtures of benzyl bromide with **2** in $CDCl_3$ which indicated significant changes to the indole and amide NH resonances; the indole NH resonances shifted from 8.86 ppm (for **2**) to 8.77 ppm (**2** + benzyl bromide, $Ka \approx 15 \pm 4\ M^{-1}$) while the amide NH resonances merged with the aromatic CH signals. As shown in Fig. 6, the aromatic CH (of **2**) signals sandwiched between the two amide NH groups (for **2**) shifted downfield to 8.52 ppm (from 8.37 ppm), apparently because of coordination to benzyl bromide, along with possible aromatic–aromatic interactions. In another experiment, the formation of

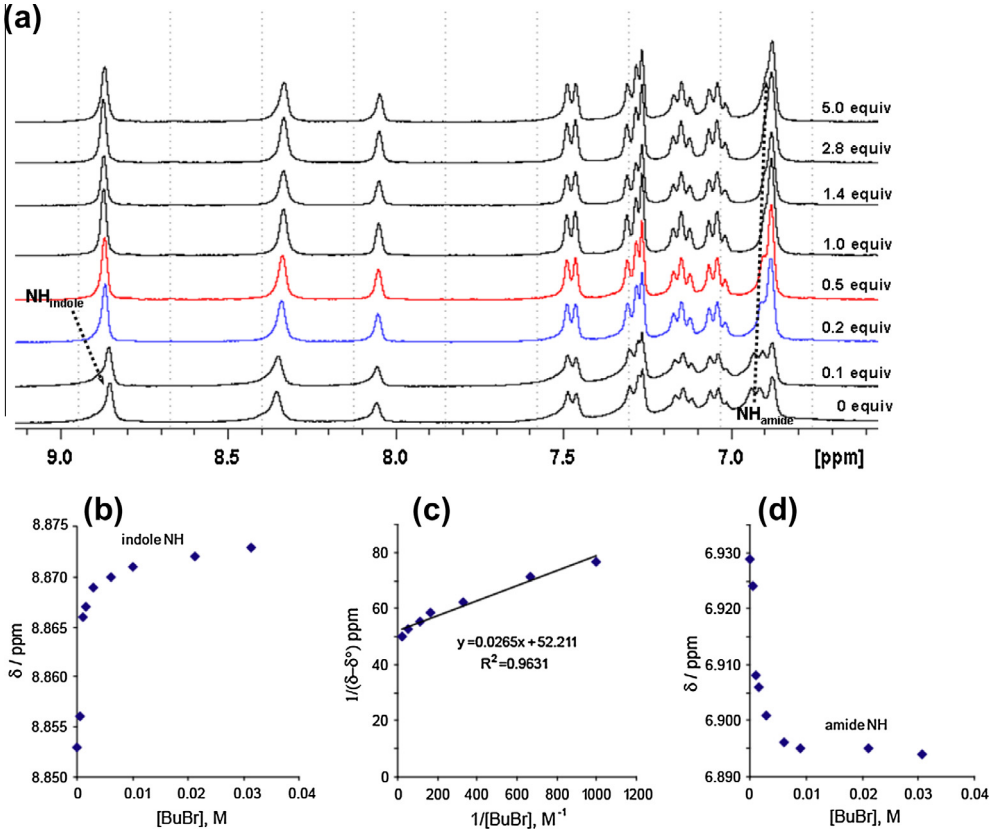


Fig. 5. Partial ^1H NMR in $CDCl_3$: (a) ligand **2** (7.0 mM) with various concentrations of bromobutane; arrow-heads indicate the chemical shifts for the indole NH and the amide NH resonances for ligand **2**. (b and c) Plots of chemical shift changes in indole NH resonances as function of bromobutane concentration, [BuBr], and the corresponding Benesi–Hilderbrand analysis, $Ka \approx 41 \pm 5\ M^{-1}$. (d) Plots of chemical shift changes for amide NH resonances vs. bromobutane concentration, [BuBr].

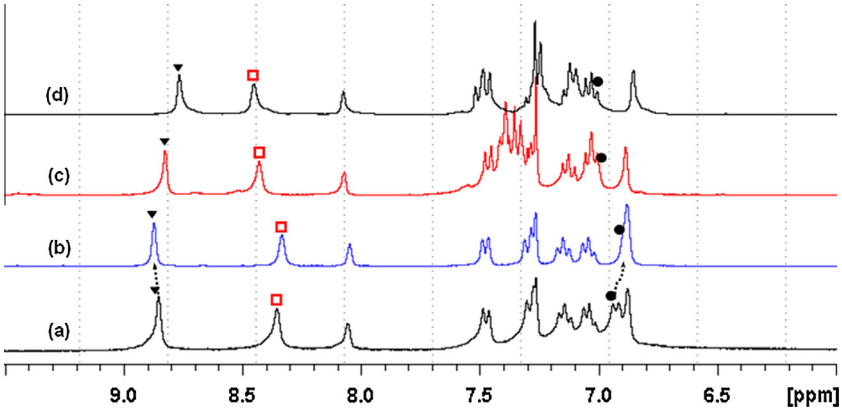


Fig. 6. Partial ^1H NMR in $CDCl_3$: (a) **2** (7.0 mM); (b) **2** + bromobutane-1 (5 equiv); (c) **2** + benzyl bromide (5 equiv); (d) **2** + bromobenzene (5 equiv) showing complexation induced chemical shifts for the indole NH (▼) and pyridine CH (□) groups; the amide NH (•) resonances merge into the aromatic resonances.

bromobenzene complex with **2** caused the indole NH group to shift upfield from 8.857 to 8.829 ppm (Fig. 6), and this corresponded to $Ka \approx 25 \pm 5\ M^{-1}$. In addition, we found that the binding of bromobenzene to **2** affected the amide NH and the aromatic CH (of **2**) resonances to shift downfield to 7.04 ppm and 8.52 ppm respectively. Notwithstanding the modest association constants obtained under the given conditions, our investigations show that in chloroform the tryptophan ligands does coordinate to organic bromides through the indole NH and amide NH groups.

In summary, we have synthesized and characterized two bis-tryptophan ligands, **1** and **2**, that can coordinate to bromide anions as well as selected organic bromides. In case of ligand **1**, the addition of bromide anion caused the amide indole NH and amide NH resonance to shift downfield, wherein the interactions were relatively weak. In comparison, **2** was apparently a better ligand for bromide anions and coordinated through the amide NH and CH groups. With neutral organic bromide molecules, ligands **1** and **2** presented surprisingly contrasting pictures; in this situation ligand **1** did not respond, while **2** demonstrated remarkable ligating ability towards the organic bromides. It was also evident from ^{1}H NMR results that the binding of bromobutane to ligand **2** caused the indole NH resonances to shift downfield while the amide NH indicated upfield shift. Benzyl bromide and bromobenzene also coordinated to **2**, producing unusual complexation induced shifts for the indole NH resonances with, the amide NH signals shifting downfield. We suggest that such differences for bromobutane and benzyl bromide, for instance, could be attributed to aromatic stacking interactions [1,7] of phenyl with the indole ring system. Further studies are necessary for the rational design of tryptophan-based ligands that can coordinate to neutral organic halides [7] more effectively. We believe that such studies may have profound implications in catalysis and molecular recognition, reminiscent of biomolecular systems.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.08.056.

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