

Synthesis and anion recognition of acetate ions using pyrrole- α -carboxaldehyde 2,4-dinitrophenyl hydrazone

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A pyrrole-based anion receptor (**1**) for acetate ions has been designed and synthesized. The receptor has been characterized by various chemical methods. Anion binding studies have been carried out using ¹H NMR and UV-vis spectra. The results indicate that deprotonation takes place after receptor **1** binds CH₃COO⁻. **1** exhibits high selectivity for acetate ions for complementarity between the receptor and anion. The compound may be useful in the field of sensor materials.

Anions are ubiquitous throughout biological systems; it is believed that they carry genetic information (like DNA, a polyanion) and participate in 70% of all enzymatic reactions¹⁻⁵. The design and synthesis of functionalized receptors for the development of potential chemosensors has recently gained considerable attention due to their low detection limits⁶⁻⁹. The binding of anionic species to the recognition sites leads to changes in certain properties of the receptors (such as color changes, etc.) enabling them to serve as indicators for guest association. This sensing function is generally achieved by the coupling of two well-defined parts. One is the anion-binding part employing various combinations of pyrroles, guanidiniums, Lewis acids, amides, and urea/thioureas^{1,10}. The other is the signaling subunits. The second component makes binding-induced changes into optical signals¹¹ (i.e., colour changes or fluorescence quenching or enhancement). Sensing molecules showing those changes can be built by attaching chromogenic units, or fluorescent signaling subunits¹², near the binding sites¹³. We describe herein the synthesis and anion recognition properties of the fused pyrrole derivative, pyrrole- α -carboxaldehyde 2,4-dinitrophenyl hydrazone (**1**). It contains one pyrrolic NH group and one phenylamino NH group that could function as anion binding moieties.

Experimental

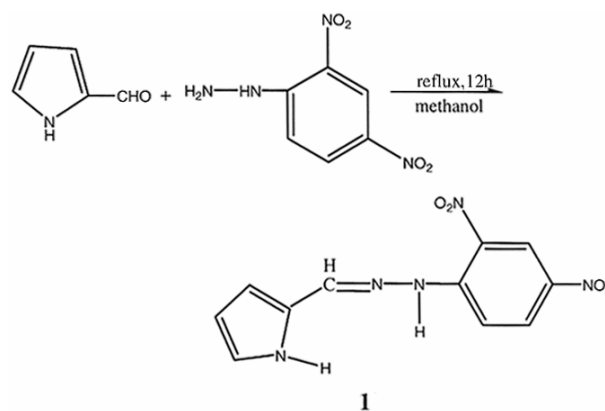
All anions, in the form of tetrabutylammonium salts were purchased from Sigma-Aldrich Chemical Co., stored in a desiccator under vacuum containing self-indicating silica, and used without any further purification. Solvents were purified prior to use and stored under nitrogen. Dimethyl sulfoxide was dried with calcium hydride and distilled at reduced pressure. Unless stated otherwise, commercial grade chemicals were used without further purification.

For synthesizing (**1**), a solution of pyrrole- α -carboxaldehyde (0.153 g) in methanol (20 mL) was added dropwise to a solution of 2,4-dinitrophenylhydrazine (0.198 g) in methanol (60 mL) with stirring and refluxed for 12 h. Then, the solvent was removed by evaporation. Recrystallization using DMF yielded red crystals. δ_{H} (400 MHz; DMSO-*d*₆; Me₄Si): 6.201 (s, 1H, Py-CH), 6.554 (s, 1H, Py-H), 7.069 (s, 1H, Py-H), 8.214 (d, 1H, J=9.6, Ar-H), 8.342 (m, 1H, J=12.4, Ar-H), 8.530 (s, 1H, Py-H), 8.873 (s, 1H, Ar-H), 11.588 (s, 1H, Py-NH), 11.701 (s, 1H, Ar-NH). Anal. Calcd for C₁₁H₇N₅O₄: C 48.00%, H 3.30%, N 25.45%, Found C 48.12%, H 3.29%, N 25.40%, MS-EI *m/z* 274.14 [(M-H)⁻, Calcd 274.18]

Unless otherwise specified, the experiments were carried out at 298±1 K. The ¹H NMR spectra were recorded on a Varian UNITY-plus 400MHz spectrometer using tetramethylsilane (TMS) as an internal standard. UV-Vis spectra were recorded on a Shimadzu UV-2450 PC spectrophotometer.

Absorption titration studies

The binding ability of receptor **1** for CH₃CO₂⁻, H₂PO₄⁻, OH⁻ and halide anions (as tetrabutyl-



ammonium salts) was investigated by UV-Vis spectroscopy in DMSO solution using a constant host concentration ($2.5 \times 10^{-5} \text{ mol.dm}^{-3}$) and increasing concentrations of anions (0–10 equiv). The change in absorbance at 495 nm for **1** was plotted against anion concentration and fitted by the equation as described by Connors¹⁴.

¹H NMR titrations

Receptor **1** ($2.50 \times 10^{-3} \text{ mol.dm}^{-3}$ in DMSO-*d*₆) was titrated against anions (tetrabutylammonium salts) by incremental addition of the anion solution in DMSO-*d*₆ such that, at the end of the titration, [1] : [anions] = 1:2.

Results and discussion

UV-vis titrations

The changes in the UV-Vis spectra of **1** upon the addition of CH_3COO^- in DMSO solution show that the absorbance changes stem from anion complexation. Peaks at 312 nm and 425 nm of **1** decrease while one new peak at 495 nm (owing to charge transfer band, CT band) is formed. Thus, the light-red color of the receptor solution turns purple-red. The colorimetric properties of the receptor (**1**) can be ascribed to the anion-induced proton transfer. (**1**) exhibits the best curve-fitting to the plot of change in absorbance against $[\text{CH}_3\text{COO}^-]$. In all cases, a 1:1 reaction stoichiometry is exhibited¹⁵. The resulting curves were analyzed by nonlinear regression methods, and the obtained equilibrium constants ($\text{LH} + \text{X}^- \rightleftharpoons \text{L}^- + \text{HX}$) are listed in Table 1.

Table 1 shows receptor **1** to exhibit best selectivity for CH_3CO_2^- over other anions. It shows that receptor **1** recognizes anions based on their sizes, and the strong electron-withdrawing $-\text{NO}_2$ substituent makes the charge delocalization easier upon interaction with CH_3CO_2^- . Massimo Boiocchi *et al.* reported¹⁶ the Log *K* values ($\text{CH}_3\text{CO}_2^- > \text{H}_2\text{PO}_4^-$) should reflect the decreasing intrinsic basicity of the anions¹⁶. These results show that the higher the negative charge of anion, the higher the tendency of forming H-bond of anion with receptor. The possible process for anion recognition is depicted in Scheme 1.

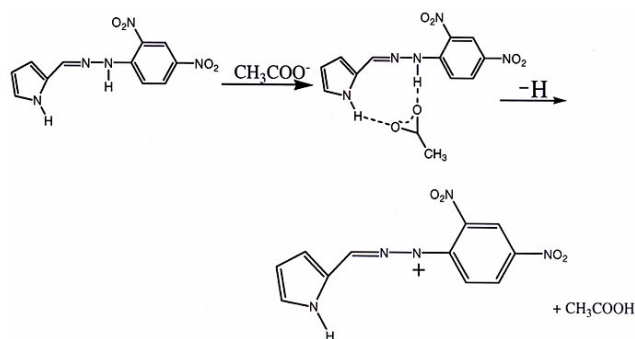
¹H NMR studies

¹H NMR was used to investigate the nature of anion coordination, and experiments were carried out in DMSO-*d*₆. Addition of tetrabutylammonium salt of

Table 1—The equilibrium constants (Logarithmic values) for receptors **1** in DMSO determined by UV-Vis absorbance titration measurements at 298 K^a

Species	CH_3CO_2^-	H_2PO_4^-	OH^-	F^-	Cl^-	Br^-	I^-
1	5.27	4.71	4	4.65	— ^b	— ^b	— ^b

^aThe anions were added as their tetrabutylammonium salts. All errors are $\pm 10\%$. ^bChanges in the UV-Vis spectra were not enough to calculate the equilibrium constant



Scheme 1

CH_3COO^- to the solution of receptor **1** in DMSO-*d*₆ resulted in ¹H NMR spectral changes, while no spectral changes were observed upon addition of tetrabutylammonium salt of Cl^- , Br^- , I^- . Also, the resonance ascribable to the NH proton of phenylamino N-H group (11.70 ppm) disappears upon successive addition of tetrabutylammonium salt of CH_3COO^- . It shows that the deprotonation takes place after receptor **1** binding to CH_3COO^- (ref. 10). In addition, new peak of the new species of the deprotonation of the NH group is not observed from the spectral window (+30 to +5.5 ppm)¹⁷. Upon binding CH_3COO^- , a broadened -NH resonance signal on the phenyl rings is noticed during the initial stages of titration. Thus, the protons of the phenyl rings of the receptor **1** that were resonating at 8.21 and 8.19 ppm as two separate doublets in the absence of CH_3COO^- slowly broaden and resonate at ~ 7.72 and 7.58 ppm in the presence of excess CH_3COO^- . In fact, two effects are expected to derive from the deprotonation, viz.: (i) The increase of electron density in the phenyl rings causes a shielding effect and should promote an upfield shift, which is expected to come from the deprotonation; and, (ii) The polarization of the C-H bonds, induced by a through-space effect¹⁸.

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