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A Novel Selective Anion Receptor for Iodide Ion: Synthesis, Characterization and Anion Binding

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A carbazole-based neutral anion receptor **3 has been designed and synthesized. Anion binding studies carried out using ¹H NMR and UV-visible reveal that this compound showed good selectivity for the iodide ion over other anions. The high selectivity for iodide ion among the anions is attributed mainly to the complementarity of the geometries between the receptor **3** and iodide ion.**

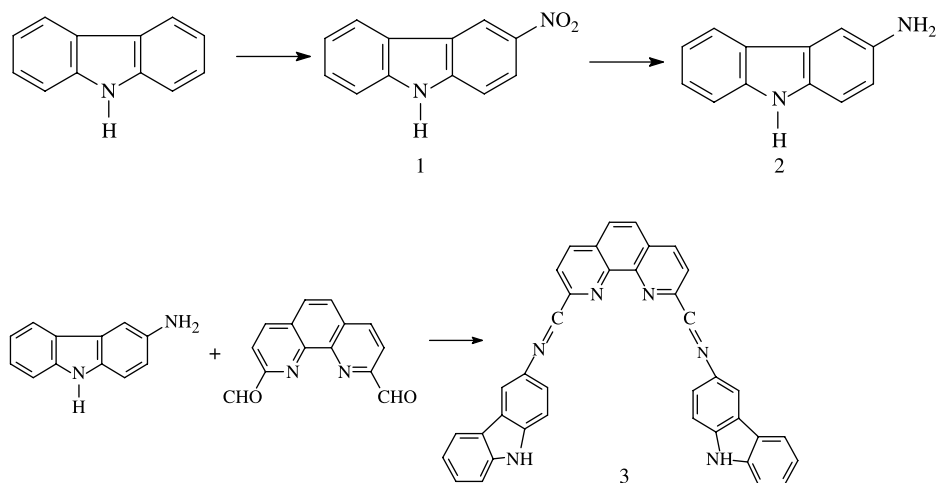
Keywords: Carbazole derivatives; Anion receptor; Iodide ion; Anion binding

INTRODUCTION

Anion recognition chemistry has attracted most interest in the last 20 years as anions play a fundamental role in a wide range of chemical and biological process, such as iodide expression in graves' disease [1,2]. Consequently numerous artificial receptors for anions have been explored [3–6]. Anionic species have a wide range of geometries, and therefore a higher degree of design may be required to make receptors complementary to their anionic guest [7]. A certain binding site may combine several of those binding groups in a proper spatial distribution for the selective coordination of target anion. Anion receptors formed complexes with the anionic guests using the noncovalent interaction, including electrostatic interaction, hydrogen bonding and hydrophobicity. Anion receptors are equipped with ammonium or guanidinium groups as binding sites which form stable host-guest complexes to iodide ion using

electrostatic force [8]. The receptor contains multiple coordination sites provided by forming (C–H)⁺–X[–] hydrogen bonds in imidazolium rings and the iodide ion and exhibits preferential coordination for spherical ones [9]. While most of the hydrogen bond anion receptors utilize (N–H)–X[–] or (O–H)–X[–] hydrogen bonds [10,11]. Herein reported is a carbazole-based neutral anion receptor (2,9-bis-(2-carbazolyl-N-iminomethylenyl)-1,10-phenanthroline) (Scheme 1). We found that the UV/vis of this receptor in DMF showed little response to the presence of F[–], Cl[–], Br[–] and acetate anions, but a high sensitivity and selectivity toward iodide ion. 1,10-phenanthroline, one of the earliest and most extensively studied bidentate ligands is widely employed as a metal-binding component in coordination chemistry, supramolecular chemistry and bioinorganic chemistry [12,13]. Its larger aromatic electron-deficient systems makes phenanthrolines an excellent π acceptor. Previously, we reported on phenanthroline-bridged diamide that exhibited a good recognition to F[–] [14]. To extend possible utility of phenanthroline, in this article, we report the synthesis and anion coordination investigation of anion receptor **3**, bearing two carbazole rings on 2,9-positions of phenanthroline. Anion receptor **3** was synthesized in 80% yield from the reaction of 2,9-dicarboxyalde-1,10-phenanthroline and 3-amino-carbazole. 2,9-Dicarboxyaldehyde-1,10-phenanthroline was synthesized according to literature [15]. 3-nitro-carbazole was prepared by the literature method [16], and by using Pd/C in ethanol solution we get the 3-amino-carbazole in 75% yield.

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SCHEME 1 The synthesis of anion receptor 3.

All compounds were characterized by ^1H NMR and elemental analyses.

EXPERIMENTAL

Reagents

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 formamide was distilled from calcium hydride. Unless stated otherwise, commercial grade chemicals were used without further purification.

Synthesis

3-Nitro-carbazole(1)

A stirred suspension of carbazole (10 g) in water (100 ml) was warmed at 40°C for an hour, while 60% nitric acid (9 ml) was added. Thereafter the temperature was raised at the rate of 10°C per hour and maintained at $80\text{--}90^\circ\text{C}$ for three hours. The dried product was digested with benzene (80 ml) for 2 hours, and the suspension quickly cooled to room temperature. The product was crystallized from glacial acetic acid; (m.p. $216\text{--}217^\circ\text{C}$) calcd for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$: C 67.92%, H 3.77%, N 13.20%; Found C 67.70%, H 3.60%, N 13.10%. ^1H NMR δ (ppm) DMSO- d_6 : 9.0 (1H, S, -NH), 8.5 (1H, S), 8.3 (1H, d), 8.2 (1H, d), 7.5 (3H, m), 7.3 (1H, m); EI-MS(M^+): 212.

3-Amino-carbazole(2)

The suspension of 3-nitro-carbazole (2 g) and Pd/C (10%) in EtOH (150 ml) was purged with H_2 for 16

hours. The mixture was filtered through a bed of Celite and the pad was washed three times with 3×20 ml of ethanol. The filtrate was evaporated in vacuum. This gave the product as the white powder. Calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_2$: C 79.12%, H 5.49%, N 15.38%; Found, C 79.00%, H 5.40%, N 15.30%. ^1H NMR: δ (ppm) DMSO- d_6 , 10.72 (1H, S, -NH), 7.90 (1H, d), 7.40 (1H, d), 7.40–7.30 (2H, m), 7.23 (1H, d), 7.08 (1H, t), 6.80 (1H, m), 4.77 (2H, S, -NH $_2$); EI-MS(M^+): 182.

2,9-Bis-(2-Carbazolyl-N-iminomethylenyl)-1,10-phenanthroline (3)

A mixture of 1,10-phenanthroline-2,9-dicarboxaldehyde (0.236 g) and 3-amino-carbazole (0.424 g) in methanol (150 ml) were stirred and refluxed for 6 hours. After cooling, the suspension was filtered giving the product as a light yellow solid, which was crystallized from DMF. calcd for $\text{C}_{38}\text{H}_{24}\text{N}_6 \cdot \text{C}_3\text{H}_7\text{NO} \cdot \text{H}_2\text{O}$: C 75.10%, H 5.04%, N 14.96%; Found, C 74.73%, H 4.60%, N 14.91%. ^1H NMR: δ (ppm) DMSO- d_6 , 11.40 (2H, S, -NH), 9.20 (2H, S), 8.70–8.66 (4H, m), 8.50 (2H, S), 8.30 (2H, d), 8.20 (2H, S), 7.70 (2H, d), 7.64 (2H, d), 7.57 (2H, d), 7.48 (2H, t), 7.26 (2H, t); FAB-MS($\text{M} + 1$): 565.

General Methods

Unless otherwise specified, all of the experiments were carried out at $298 \pm 1\text{K}$. The ^1H NMR spectra were recorded on a Varian UNITY-plus 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. UV-visible spectra were recorded on a Shimadzu UV-2450 PC spectrophotometer.

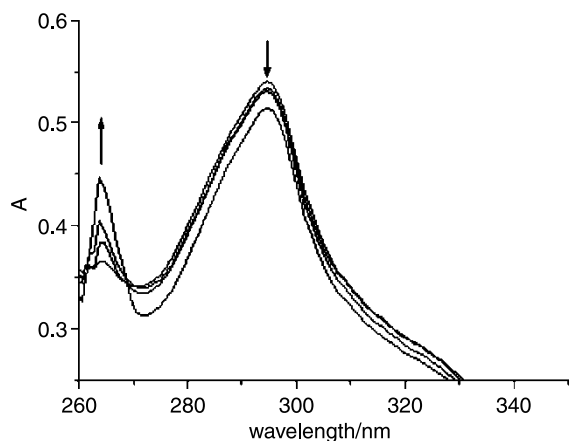


FIGURE 1 Absorption spectra of **3** in DMF in the presence of increasing concentration of I^- . The concentrations of **3** is $1 \times 10^{-5} \text{ mol L}^{-1}$, I^- exists in its $n\text{-Bu}_4\text{N}^+$ salt.

RESULTS AND DISCUSSION

UV-visible Experiments

The changes in the UV-visible spectra of the receptor **3** observed upon the addition of I^- in DMF solution indicates that the absorbance changes stem from anion complexation (Fig. 1). The peak at 294 nm of **3** decreased while a new peak at 264 nm appeared, which is the charge transfer (CT) band. The complexation ability of receptor **3** to anions was measured by standard UV/Vis titration experiments in dimethyl formamide solutions using a constant host concentration ($1 \times 10^{-5} \text{ M}$) and increasing concentration of guest anions (1–15 equiv). For all of the anions studied, only the iodide ion is capable of quenching the UV/vis intensity. The UV/vis intensity at 264 nm of **3** in DMF was gradually increased as the iodide ion concentration was increased. The stoichiometry between host and guest was determined by

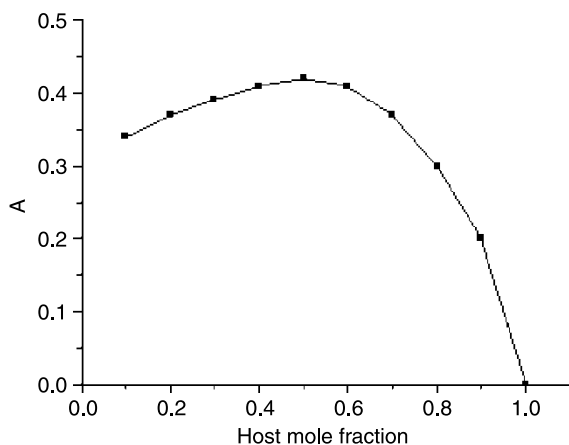


FIGURE 2 Job plot for **3** and I^- .

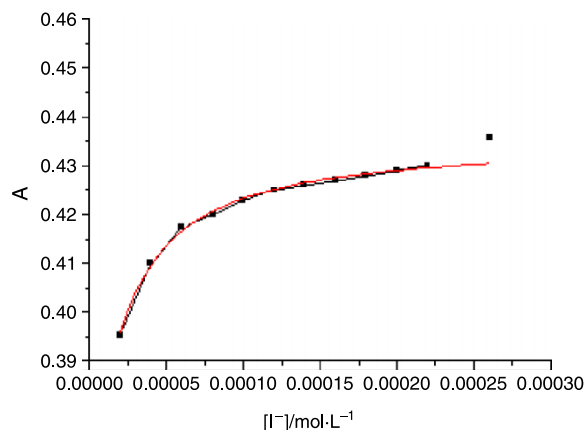


FIGURE 3 Absorbance of **3** with I^- at 264 nm. $[3] = 1 \times 10^{-5} \text{ mol L}^{-1}$, I^- exists in its $n\text{-Bu}_4\text{N}^+$ salt (solid line in figure is fitting curve).

UV-visible Job plot, giving the receptor/iodide stoichiometry of 1:1 (Figs. 2 and 3). The resulting bind curves were analyzed by nonlinear regression methods, and the association constants listed in Table I [17].

^1H NMR Experiments

In order to investigate the nature of anion coordination, ^1H NMR experiments were carried out in $\text{DMSO-}d_6$. A partial ^1H NMR spectrum is shown in Fig. 4. As expected, we observed the ^1H NMR spectrum changes on addition of 1 equiv of the tetrabutylammonium salts of I^- in $\text{DMSO-}d_6$. The intensity of proton signals of NH in carbazole rings decreased as the addition of iodide. From which we presume that the two N–H in carbazole rings participated in the formation of the hydrogen bonds (see Fig. 4).

Computational Methods

The molecular complexes of **3** with iodide ion were examined by density functional calculations. Geometry optimizations were performed at the B3LYP level using the split-valence polarized 6-31G* basis set ($E = 68 \text{ A.U.}$). All calculations were performed using the Gaussian 98 series of programs [18].

TABLE I Anion binding constants (M^{-1}) for receptors **3** in DMF determined by UV-visible absorbance titration measurements at 298 K^\dagger

Species	F^-	Cl^-	Br^-	I^-	CH_3COO^-
3	‡	‡	‡	5×10^4	‡

† The anions were added as their tetrabutylammonium salts. All errors are $\pm 10\%$. ‡ Changes in the UV-visible spectra were not enough to calculate the binding constant

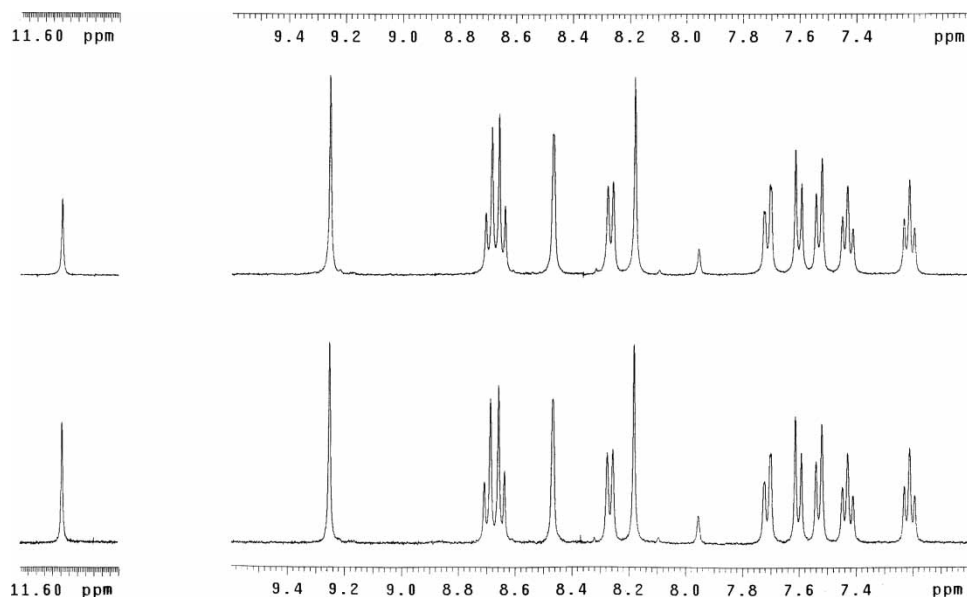


FIGURE 4 Partial ^1H NMR spectra (500 MHz, $\text{DMSO-}d_6$, 298 K) (a) host **3**; (b) host **3** + 1 equiv of I^- .

Molecular modeling showed that the anion receptor **3** has a rigid cavity. The two N-H-X^- in carbazole rings form a cavity and the shape of the cavity seemed to be suitable size for spherical ions. From modeling, the distance between the two hydrogen of N-H in carbazole rings are 8.2 \AA , which enable receptor **3** to bind larger anions well, such as iodide. Average distance from receptor amide nitrogen to bound iodide ion are $3.67\text{--}3.71 \text{ \AA}$ [19], the cavity is more complementary to the size of the iodide ion than the size of other anions. It is important to note that the carbazole NH protons bear a strong charge (0.405). Thus, the receptor **3** is characterized by strong hydrogen-bond donor groups. There are two

carbazole NH protons facing each other that could function as anion binding moieties (Figs. 4 and 5).

CONCLUSION

In summary, we have designed and synthesized a neutral receptor with a rigid spacer, which displays selectivity for the iodide ion over other anions. This anion receptor is characterized by strong hydrogen-bond donor groups, that two carbazole NH protons bear a strong charge (0.405) like the "claw" (i.e., structures with two carbazole NH protons facing each other).

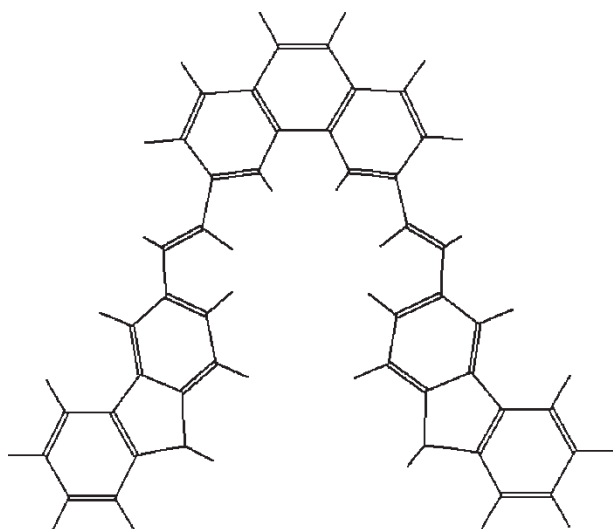


FIGURE 5 The energy minimized structure of the receptor **3**.

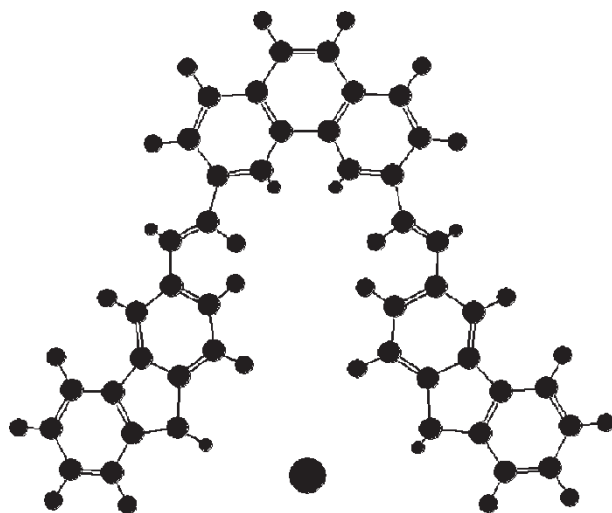


FIGURE 6 The energy minimized structure of the complex 1:1 the receptor **3** and iodide.

Acknowledgements

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