



Employing a hydrazine linked asymmetric double naphthalene hybrid for efficient naked eye detection of F⁻: Crystal structure with real application for F⁻

Arghyadeep Bhattacharyya, Subhash Chandra Makhal, Soumen Ghosh, Nikhil Guchhait *

Department of Chemistry, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, India

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ABSTRACT

An asymmetric hydrazide, **(12E, 13E)-2-((naphthalen-1-yl) methylene)-1-(1-(2-hydroxynaphthalen-6-yl) ethylidene) hydrazine** (abbreviated as **AH**) is synthesized and characterized by standard techniques and crystal structure of **AH** has been obtained. The naked eye detection of F⁻ in aqueous acetonitrile (acetonitrile: water = 7:3(v:v)) by **AH** has been investigated by UV-Visible titration and in presence of other anions, the limit of detection being 1.31×10^{-6} (M). The mechanism of F⁻ sensing has been explored by ¹H NMR titration. **AH** undergoes hydrogen bonding with F⁻ followed by deprotonation. The practical utility of **AH** has been explored by successful test kit response and color change in toothpaste solution.

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1. Introduction

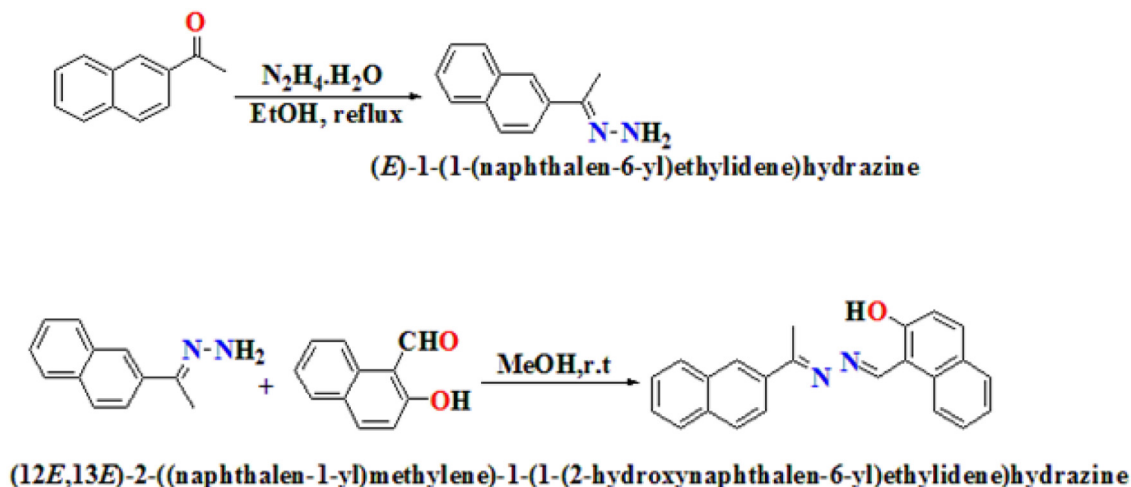
The incessant surge in industrial development has dearly affected the environment, jeopardizing flora and fauna alike. The alarming rate of increment in environmental pollution has led scientists, chemists in particular, to adopt cheap and effective means of detection and subsequent removal of agents which bring about environmental pollution. A close look at the anionic pollutants present in water reveals an interesting 'two-faced' property of fluoride. On one hand, it plays an important role in preventing dental caries and treatment of osteoporosis when ingested within permissible limits [1,2]. In addition, the industrial as well as pharmaceutical importance of fluoride cannot be neglected due to its presence in cockroach poisons as well as in hypnotic and anesthetic drugs [3–5]. On the other hand, an excess intake of fluoride opens up an array of physiological disorders, fluorosis being the most deadly, followed by thyroid activity depression and bone disorders [6–8]. Apart from the Indian subcontinent, China and Africa are reported to be countries affected majorly by fluoride pollution [9]. According to reports; more than forty blocks of seven districts of West Bengal are endemic to fluorosis with approximately health of 66 million people at stake [10]. It is at this juncture, the utility of smart synthesized chemical tools to detect fluoride can be fathomed.

Over the years, innumerable chemosensors for detecting fluoride involving Schiff bases containing suitable electron withdrawing groups

have been reported [11,12]. Between colorimetric and fluorescent receptors for detection of fluoride, the former enjoys greater attention due to the innate simplicity involved with the technique itself. Quite monotonously, bulk share of recent reports utilize dinitrophenylhydrazones for colorimetric detection of fluoride [13–15] which is quite obvious due to the strongly acidic hydrogen present in the dinitrophenylhydrazine moiety itself. Our group has been involved in the detection of anions by very simple molecules, asymmetric acyl hydrazones and reduced Schiff bases being provided the maximum importance [16–18]. Following our line of work, in the current report we explore the colorimetric Fluoride detection ability of an asymmetric double naphthalene receptor, **(12E, 13E)-2-((naphthalen-1-yl) methylene)-1-(1-(2-hydroxynaphthalen-6-yl) ethylidene) hydrazine**, abbreviated as **AH**. Receptor **AH** is the first of its kind as it involves two asymmetric naphthalene units on both sides of a Hydrazine linkage. Number of such reports involving asymmetric hydrazine linkage utilized for anion detection is few in literature. Receptor **AH** has been synthesized and characterized by NMR, FTIR, ESIMS and XRD techniques. Receptor **AH** can detect fluoride by a sharp change in color from greenish yellow to orange in semi-aqueous medium (acetonitrile: water = 8:2, v:v) up to a low detection limit of 1.314×10^{-6} (M). The mechanism of colorimetric detection involves Hydrogen bonding with F⁻ followed by deprotonation of phenolic hydrogen present in **AH**. The practical utility of **AH** has been demonstrated by successful paper strip response as well as detection of fluoride in commercially available toothpaste. Thus, the current report could be a potential tool for cheap and effective fluoride detection.

* Corresponding author.

E-mail address: nguchhait@yahoo.com (N. Guchhait).



Scheme 1. Synthetic route to receptor AH.

2. Experiment

2.1. Reagents and Apparatus

2-Acetyl naphthalene, 2-hydroxy naphthaldehyde, hydrazine hydrate and Tetrabutylammonium salts of anions were purchased from Sigma-Aldrich and used without further purification. Spectroscopic grade acetonitrile and double distilled water was used for naked eye response to anions as also for UV–Visible titrations. ^1H NMR and ^{13}C NMR were recorded on Bruker Advanced Supercon 300 MHz and chemical shifts are expressed in ppm using TMS as internal standard. IR spectrum was recorded on Perkin Elmer spectrum-100 and UV–Vis titrations and related experiments were conducted in Hitachi U-3501 Spectrophotometer. Mass spectrum was recorded on Waters Xevo G2-S Q TOF mass spectrometer. The single crystal of compound **2** was mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo K_{α} ($\lambda = 0.71073 \text{ \AA}$) radiation. The crystal was placed 60 mm from the CCD and 360 frames were measured with a counting time of 5 s. The structure was solved using the Patterson method using SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non hydrogen atoms. Non hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non hydrogen atoms. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using SADABS program. All

calculations were carried out using SHELXS 97, PLATON 99, ORTEP-32 and WinGX system Ver-1.64 [19].

2.2. Synthesis of AH

The synthesis of **AH** was achieved in two steps (Scheme 1):

2.2.1. Synthesis of (E)-1-(1-(Naphthalen-6-yl) Ethylidene) Hydrazine: (E)-1-(1-(Naphthalen-6-yl) Ethylidene) Hydrazine (**1**)

1 was synthesized using procedure reported elsewhere and characterized using ^1H (ESI, Fig. S1) and ^{13}C (ESI, Fig. S2) NMR respectively.

2.2.2. Synthesis of (12E, 13E)-2-((Naphthalen-1-yl) Methylene)-1-(1-(2-Hydroxynaphthalen-6-yl) Ethylidene) Hydrazine (**AH**)

0.18 g of **1** (~1 mmol) was dissolved in dry methanol and stirred rapidly for 5 min to render homogeneity to the solution. An equimolar methanolic solution of 2-hydroxy naphthaldehyde was added drop wise to the aforesaid solution and stirred at room temperature for 2 h. The bright yellow crystalline solid thus formed was filtered under suction, washed 3–4 times with cold methanol and dried under vacuum overnight. The solid was then characterized by FTIR, ^1H NMR, ^{13}C NMR, ESIMS and its structure was finally confirmed by XRD analysis to be the desired product **AH**. IR (KBr, cm^{-1}): 3500, 1620.60, 1590.18, 1573.99, 817.04, 741.73. ^1H NMR (300 MHz, DMSO d_6 , 290 K, TMS): 13.41 (s, 1H, —OH), 9.77 (s, 1H, —CH=N), 8.53–8.58 (m, 2H, Ar—H), 8.28 (s, 1H, Ar—H), 7.90–8.04 (m, 5H, Ar—H), 7.60 (s, 3H, Ar—H), 7.43 (d, 1H, Ar—H), 7.26 (d, 1H, Ar—H), 2.65 (s, 3H, methyl-H) (ESI, Fig. S3), ^{13}C NMR (300 MHz, DMSO d_6 , 290 K, TMS): 164.95, 160.92,

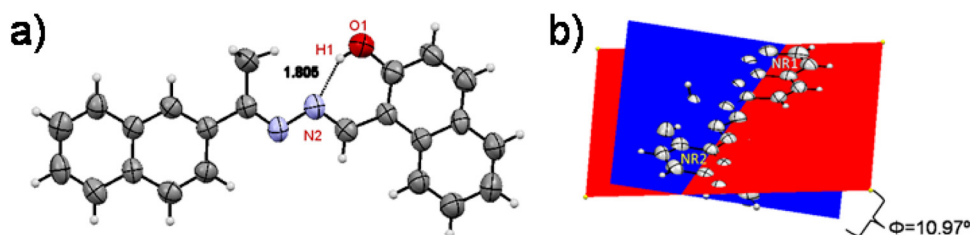


Fig. 1. a) Intramolecular H-bonding in **AH** and ii) plane between two naphthalene rings; denoted NR1 and NR2.

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