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Synthesis and structural X-ray analysis of 1,1'-(naphthalene-1,8-diyl)-3,3'-dibenzoyl-bisthiourea and its use as anion-binding receptor

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A novel artificial receptor, 1,1'-(naphthalene-1,8-diyl)-3,3'-dibenzoyl-bisthiourea, based on a 1,8-naphthalene skeleton bearing bisthiourea groups was prepared and characterized by IR and ^{1}H-NMR, ^{13}C-NMR, and MS spectroscopic techniques. The compound proved to be an efficient and selective naked-eye detector for the fluoride, cyanide, and hydroxide ions in DMSO. The crystal structure of the title compound was examined by using X-ray crystallographic techniques and found to be crystallized in the monoclinic space group $P-1$ with the unit cell parameters: a = 8.1556(8) Å, b = 12.0127(11) Å, c = 13.2081(11) Å, α = 109.510(7)°, β = 95.390(7)°, γ = 103.660(7)°, Z = 2. The intramolecular N-H$\cdots$O hydrogen bonding interactions between the N-H and the oxygen atom of C=O groups support a 1,1'-(naphthalene-1,8-diyl)-3,3'-dibenzoyl-bisthiourea framework. Moreover, the combinations of N—H$\cdots$S bonds produce R_2^2 (8)rings.

Key Words: 1,1'-(Naphthalene-1,8-diyl)-3,3'-dibenzoyl-bisthiourea, anion-binding receptor, crystal structure, bisthiourea

Introduction

Studies of N-aryl-N-benzoyl-thiourea compounds have attracted increasing attention due to their potential use in agriculture for their insecticidal, herbicidal, and pesticidal activities;[1–4] in medicine for their antibacterial

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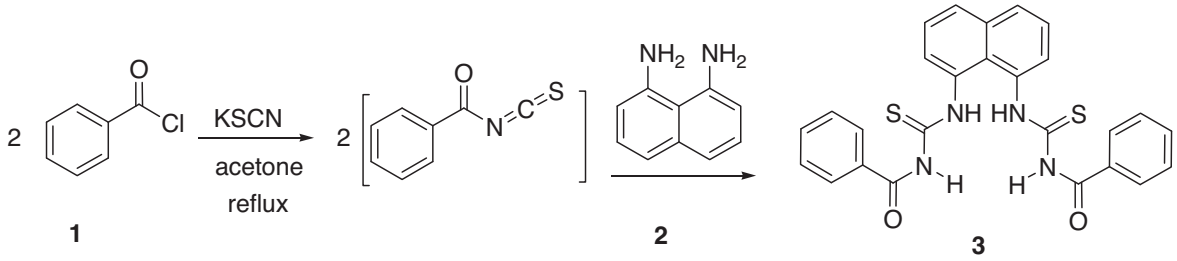
and antimicrobial activities;[5,6] and in analytical chemistry for extraction and separation.[7,8] The bioactivities of many acyl thiourea compounds have a promoting effect on plant growth.[9] Furthermore, aroyl and acyl thiourea derivatives are attractive model compounds for studies in solid-state chemistry due to their tendency to form intra- and intermolecular hydrogen bonds of the N-H proton-donor groups to sulfur and carbonyl oxygen atoms.[10–13]

Anions are of crucial importance in a range of biological, chemical, medical, and environmental processes. Therefore, synthetic molecular receptors for anions have received considerable attention in recent years.[14] These receptors are usually based on macrocyclic ammonium/guanidinium,[15] amides,[16] urea/thiourea,[17–19] functionalized calixarenes,[20] aromatics such as pyrroles,[21] carbazoles and indoles,[22] and phenylhydrazones.[23,24] They exhibit such an obvious color change when anion is added that they can be detected by the naked eye without the need to resort to spectroscopic instrumentation.[25] Many synthetic receptors have been reported, especially for F^- anion in the presence of Cl^-, Br^-, and I^- ions.[26] Recently, among a variety of possible hydrogen bond donor groups, systems employing thiourea moieties have been proven to be very efficient in the design of neutral anion binding receptors.[27,28]

In this work, we present the synthesis (Scheme 1), X-ray analysis, and characterization and structural analysis of 1,1'-(naphthalene-1,8-diyl)-3,3'-dibenzoyl-bisthiourea. Its structure was confirmed by several spectroscopic techniques, namely IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy and mass analysis. Its structure was also confirmed by single crystal X-ray diffraction structural analysis. The location of the group on the bis-thiourea moiety regarding intra- and intermolecular hydrogen bonding interactions between molecules in its crystal structure has been discussed. In addition, this compound exhibited a distinct color change in the presence of fluoride anions, and showed no response to the other halide anions. It also responded to cyanide (CN^-) and hydroxide (OH^-) ions.



Scheme 1. Synthesis of 1,1'-(naphthalene-1,8-diyl)-3,3'-dibenzoyl-bisthiourea.

Experimental section

Apparatus

Melting points were measured on an Electro Thermal IA 9100 apparatus using a capillary tube. The ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker NMR spectrometer operating at 400 and 101.6 MHz. The UV-Visible spectra were recorded using a Perkin-Elmer WinLab-25 series spectrophotometer with a quartz cuvette (path length: 1 cm). Infrared absorption spectra were obtained by a Perkin Elmer BX II spectrometer as KBr disks and were reported in cm^{-1} units. MS spectra were recorded on an Agilent 5973 Inert Mass Selective Detector equipped with a direct insertion probe.

Reagents

All reagents for synthesis were obtained commercially and were used without further purification. In the titration experiments, all the anions were added in the form of tetra-n-butylammonium (TBA) salts, which were purchased from Merck Chemical Co. and Acros Organics, stored in a vacuum desiccator containing self-indicating silica and fully dried before use. Dimethyl sulfoxide was dried with calcium hydride and then distilled at reduced pressure.

Synthesis of the compound

A mixture of benzoyl chloride (2.32 mL, 20 mmol) and KSCN (1.94 g, 20 mmol) in 20 mL of acetone was refluxed under stirring for 1 h; then a solution of 1.58 g (10 mmol) of 1,8-diaminonaphthalene in 20 mL of acetone was added dropwise to benzoyl isothiocyanate over 0.5 h at ambient temperature. When the solution was added completely, the resulting solution was then mixed for 5 h at ambient temperature and the progress of the reaction was controlled by TLC. After the reaction was completed, the solution was poured into a beaker containing an ice-water mixture. The white precipitate was filtered and washed with distilled water several times and then dried under vacuum. Recrystallization of the crude product in tetrahydrofurane gave pure colorless crystals.

Characterization

Analytical and spectral data

Yield: 3.85 g, 80%. colorless crystal, mp 222-224 °C; IR (KBr pellet), (cm^{-1}): 3394, 3186 ($N-H$), 3120, 3045 (C_{arom} -H), 1685 ($C=O$), 1256 ($N-C$=S, thioureido), 712 ($C=S$); ^{1}H-NMR ($CDCl_3$): δ ppm: 12.52 (s, 2H, N-**H**), 11.49 (s, 2H, N-**H**), 8.82-7.27 (8H, symmetric Ar-**H**); ^{13}C-NMR ($CDCl_3$) δ ppm: 183.4 (C=S); 169.0 (C=O), 143.4, 133.7, 130.3, 129.3, 128.9, 126.7 ($C_{Ar.}$); MS (EI): (m/z) = 484 (M+1).

Absorption titration studies

All anions such as F^-, Cl^-, Br^-, I^-, CN^-, and OH^- were added in the form of tetrabutylammonium salts to 5×10^{-5} M solutions of the title host compound in DMSO. The binding properties of the title compound toward F^- were explored with UV-Vis titration (Figure 3) and the ^{1}H-NMR experiment (Figure 4).

Results and discussion

The title compound, 1,1'-(naphthalene-1,8-diyl)-3,3'-dibenzoyl-bisthiourea, was characterized by MS analysis, IR, and ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques as well as single crystal X-ray diffraction analysis.

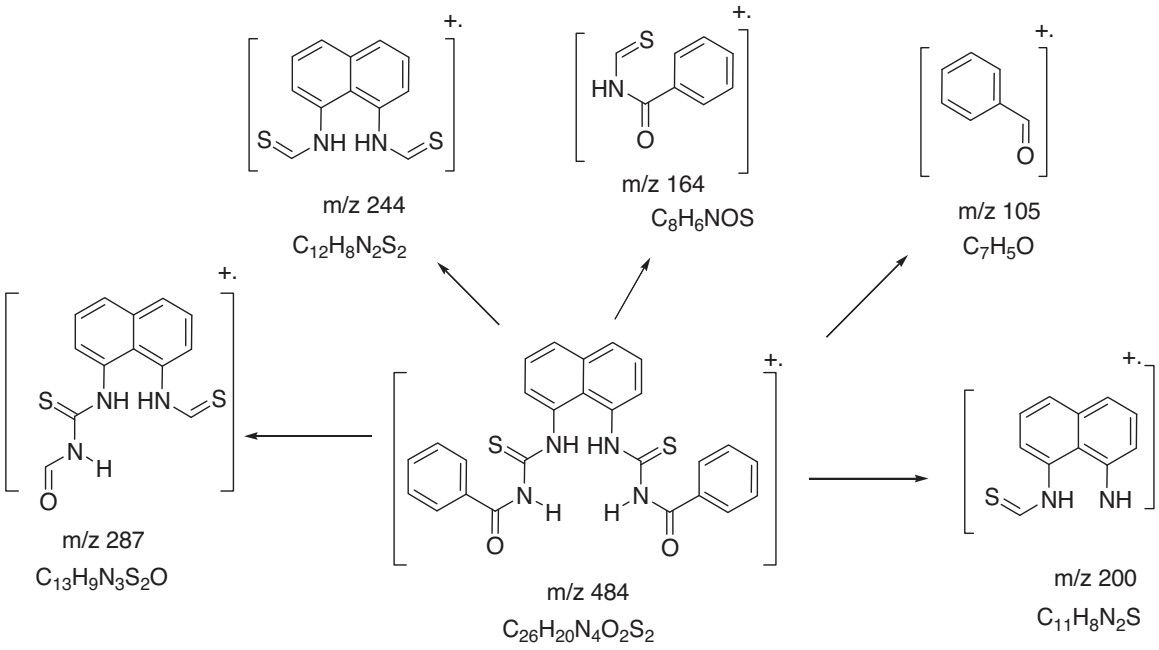
Spectroscopic studies

The IR spectrum of the title compound exhibited 2 N-H stretching bands at 3186 and 3394 cm^{-1} in the high energy region. C-H stretching vibrations from aromatic groups such as phenyl and naphthalene are observed in

the 3120 and 3045 cm^{-1} range. In the 700-1700 cm^{-1} region, a strong absorbance band in the IR spectra of the compound appears at about 1685 cm^{-1}, apparently decreasing in frequencies compared with the ordinary carbonyl absorption (1700 cm^{-1}). This is interpreted as being a result of its conjugated resonance with the phenyl rings and the possible formation of hydrogen bonding with N-H. The strong bands observed at 1255 and 713 cm^{-1} were respectively assigned to thioureido N-C=S and C=S stretching vibrations[29] (see Figure 7).

The experimental ^{1}H-NMR data of the title compound correspond to those of similar compounds.[11–13] In the NMR spectra of the title compound, 2 signals were noted as singlets at 12.52 and 11.49 ppm, assigned to the NH proton. The resonance values of the N-H protons are interpreted as being a result of conjugated resonance with the carbonyl and thiocarbonyl, respectively. The resonance values of the aromatic protons for naphthalene-1,8-diyl ring and phenyl rings were 8.82-8.05 ppm and 7.14-7.21 ppm as expected, respectively. The most deshielded in the ^{13}C-NMR signals correspond to C=O and C=S groups. The carbon atom of carbonyl appears at 169 ppm, while the carbon atom of thiocarbonyl appears at 183 ppm due to the lower excitation energy $\pi - \pi^*$. Formation of intramolecular hydrogen bonding, the increasing electronegativity of oxygen and sulfur atoms, and different environments such as phenyl and naphthalene-1,8-diyl conformations cause a deshielding effect for these signals. These data agree with the results reported by Arslan et al.[30]

The mass spectral fragmentation pattern of the title compound is depicted in Scheme 2. Values of the molecular ion peak at 484 and fragment ion peaks at 287, 244, 200, 164, and 105 confirmed the presence of bisthiourea (see Figure 8).



Scheme 2. The mass spectral fragmentation pattern of compound.

UV-Vis experiments

Firstly, the anion binding affinity of the present thiourea-based receptor was determined by UV-Vis absorption spectroscopy in the absence and presence of different anions such as F^-, Cl^-, Br^-, I^-, CN^-, and OH^- (as

tetrabutylammonium salts). The experiment was performed by preparing 5×10^{-5} M solution of receptor in DMSO solution followed by addition of particular tetrabutylammonium anionic salts separately. In the absence of anions, the weak absorbance band at 287 nm was ascribed to $\pi - \pi^*$ transition of bisaroylthiourea. Upon the addition of F^-, CN^-, and OH^- to receptor, a prominent change was observed in UV-Vis absorption spectra. In contrast, addition of an excess of tetrabutylammonium salt of Cl^-, Br^-, and I^- did not cause any notable spectrum changes (see Figure 1). The observed color changes in the presence of F^-, OH^-, and CN^- also could be detected by the naked eye (see Figure 2). Secondly, hydrogen binding ability of the receptor for F^- was investigated by UV-Vis spectrometry in DMSO using a constant host concentration (5×10^{-5} M) and increasing concentrations of the F^- (0–5 equivalence). The UV-vis spectrum of the receptor (5×10^{-5} M) in DMSO had a characteristic absorption peak at 287 nm. With the addition of more and more doses of fluoride ions, the color of the receptor solution changed from colorless to yellow; at the same time, the intensity of the absorbance band at 287 nm decreased gradually and that of the absorbance band at 335 nm increasing gradually (see Figure 3). Obviously, a distinct isosbestic point at 308 nm was observed during the titration process between the receptor and F^- ion, which clearly indicated the formation of complex between receptor and F^- ion.[26] By increasing the fluoride ion concentrations, the corresponding changes in absorbance intensities at 335 nm were plotted against anion concentrations. The binding constant of the complex formed between receptor and F^- ion was calculated by nonlinear fitting of the spectroscopic titration curve[31] as log K_{ass} 3.95 ± 0.13 (Figure 3).

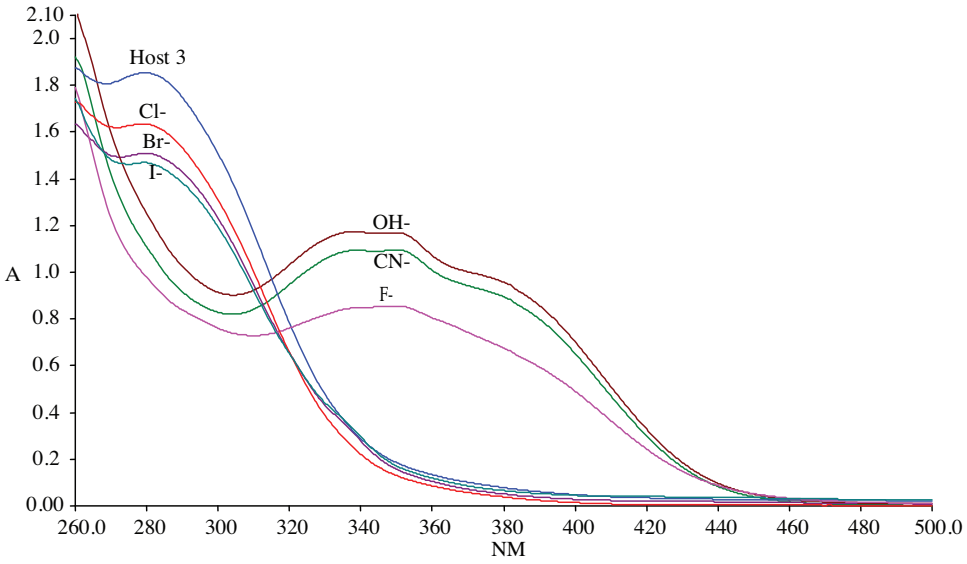


Figure 1. UV-vis spectra of 3 (5×10^{-5} mol L^{-1}) after addition of different anions (none, F^-, Cl^-, Br^-, I^-, CN^-, OH^-) in DMSO.

^{1}H-NMR experiments

There are 2 kinds of NH proton signals for the free compound, designated as CONH (12.51 ppm) and CSNH (11.49 ppm) (as shown in Scheme 1 and Figure 4). The hydrogen binding of F^- ion to the free compound

was investigated by monitoring the changes in the ^{1}H-NMR spectra of DMSO-d_6 solution of the receptor upon addition of F^- (1, 2 equiv.). The thiourea N–H signals at 12.51 and 11.49 ppm disappeared with the addition of 1.0 equiv. F^- ion solution and a new broad and small band at 10.88 ppm appeared. However, this new band completely disappeared with the addition of 2.0 equiv. of the ion solution (Figure 4). The results indicate that there are 2 steps in anion recognition: anion hydrogen bonds with receptor and deprotonation of it takes place due to fluoride ion, which is a strong base with a high charge density and small size.[32]

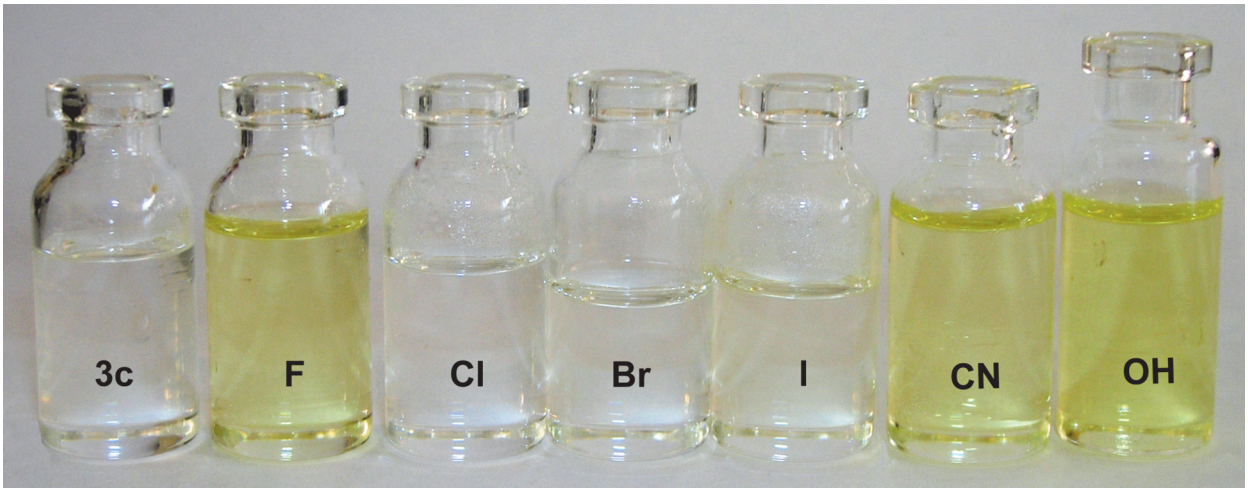


Figure 2. Color changes in 3 (5×10^{-5} mol L^{-1}) after addition of different anions (none, F^-, Cl^-, Br^-, I^-, CN^-, OH^-) in DMSO, from left to right.

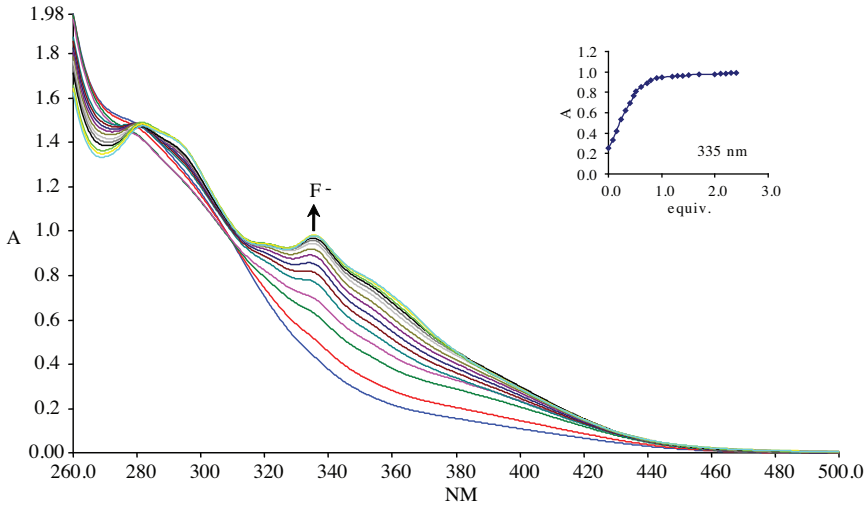


Figure 3. Titration of 5×10^{-5} mol L^{-1} solution of **3** in DMSO with a standard solution of F^- (as tetrabutylammonium salt) in DMSO at 298.2 ± 0.1 K.

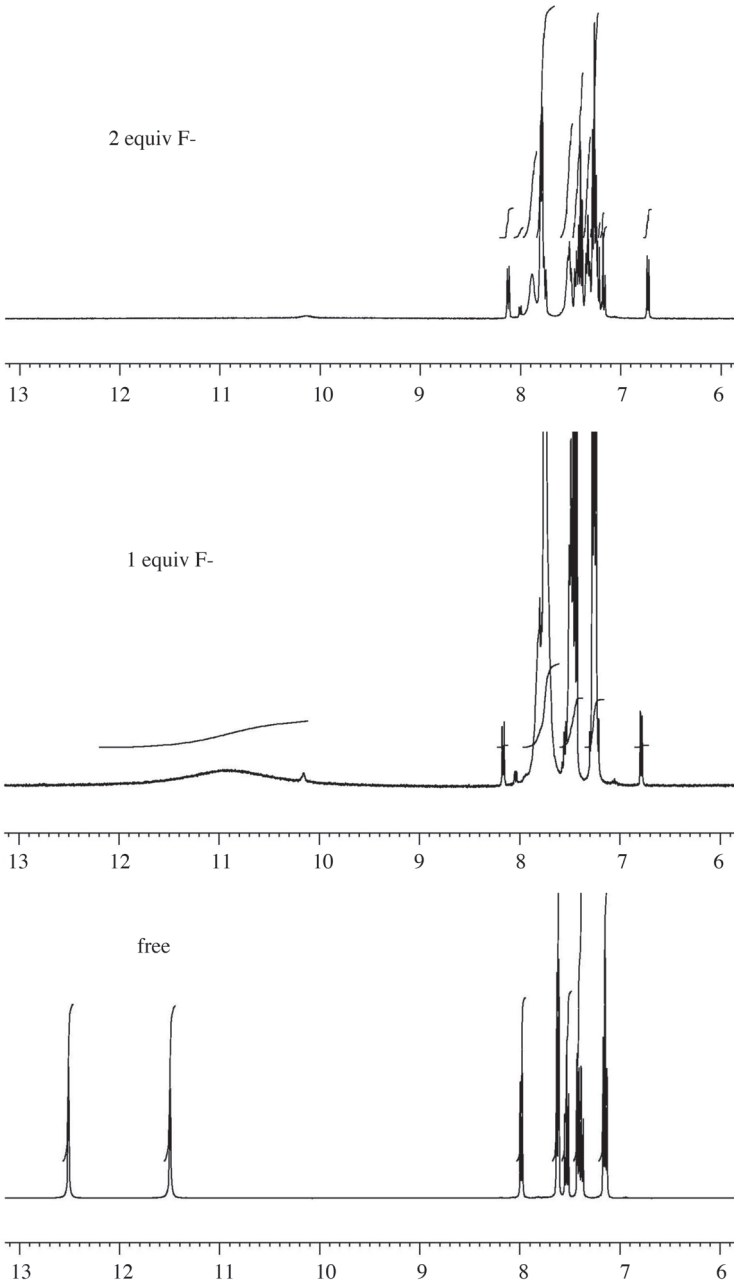


Figure 4. Partial ^{1}H-NMR (400 MHz) spectra of the receptor (5×10^{-5} mol L^{-1}) in DMSO-$d6$; in the absence and in the presence of 1 and 2 equiv. of $[(t-Bu)_4N]F$.

X-ray crystallography

A suitable colorless prism-shaped crystal sample of size 0.51 × 0.38 × 0.21 mm was chosen for the crystallographic study and then carefully mounted first on a glass fiber and then on the goniometer of a STOE

diffractometer with an IPDS(II) image plate detector. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Reflection data were recorded in rotation mode using the ω scan technique by using X-AREA[33] software. Unit cell parameters were determined from least-squares refinement of setting angels with θ in the range $1.7 \leq \theta \leq 27.2$. The structure was solved by direct methods using SHELXS-97[34] implemented in the WinGX[35] program suite. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the nonhydrogen atoms, or equivalently corresponding to 307 crystallographic parameters, using SHELXL-97.[36] All H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.86 and 0.93 Å for NH and CH atoms, respectively. The displacement parameters of the H atoms were fixed at U_{iso}(H) = 1.2 U_{eq} of their parent atoms. Data collection: X-AREA; cell refinement: X-AREA; data reduction: X-RED32.[37]

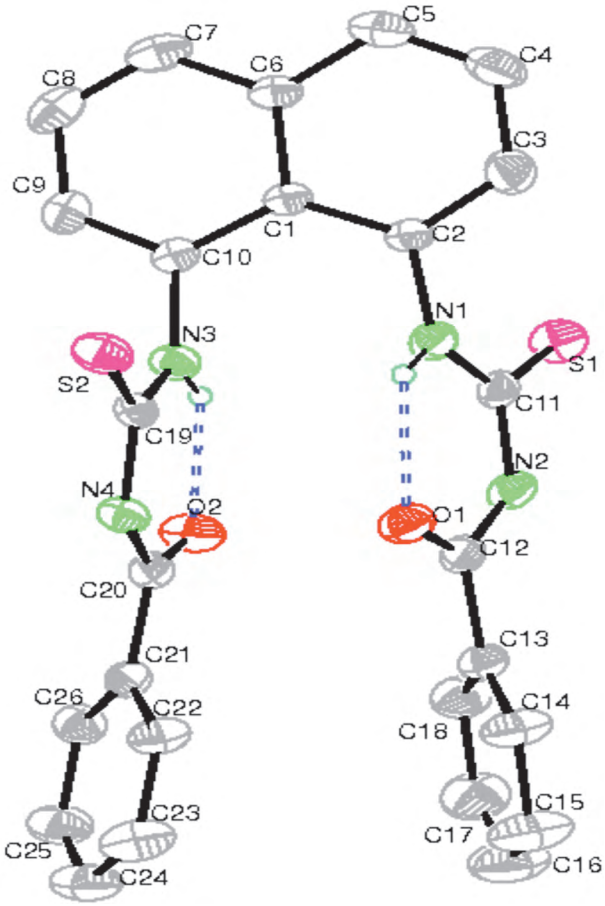


Figure 5. Molecular structure of the title compound showing the atomic labeling.

Crystal structure and conformations

Details of crystal structure crystal data collection and refinement of the title compound are summarized in Table 1. The selected bond lengths and bond angles for the title compound are listed in Tables 2 and 3. The ORTEP and molecular packing diagrams are displayed in Figures 5 and 6.

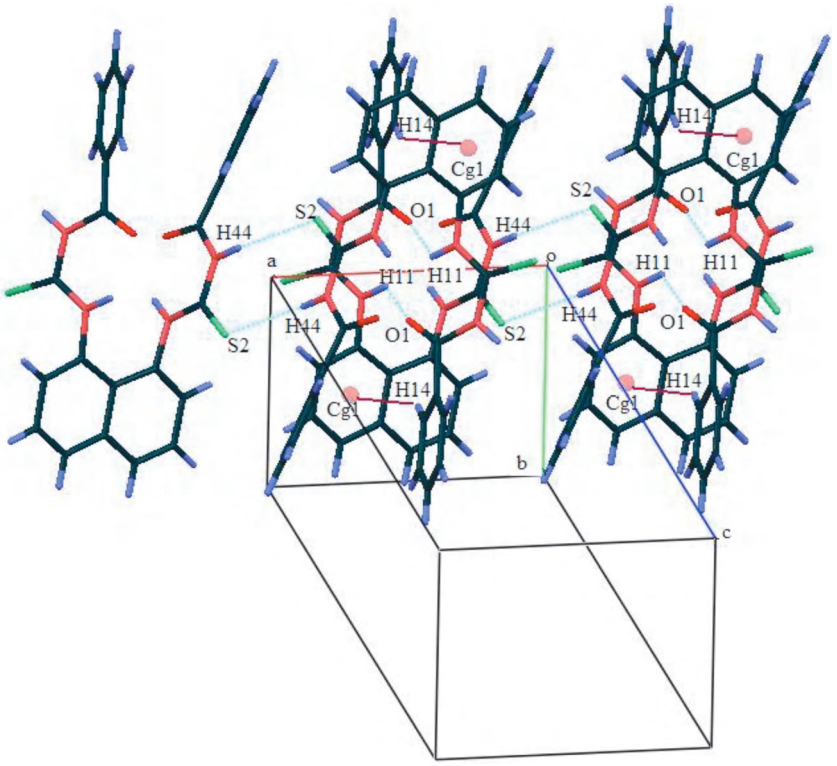


Figure 6. Packing diagram for the title compound with hydrogen bonds as dotted lines.

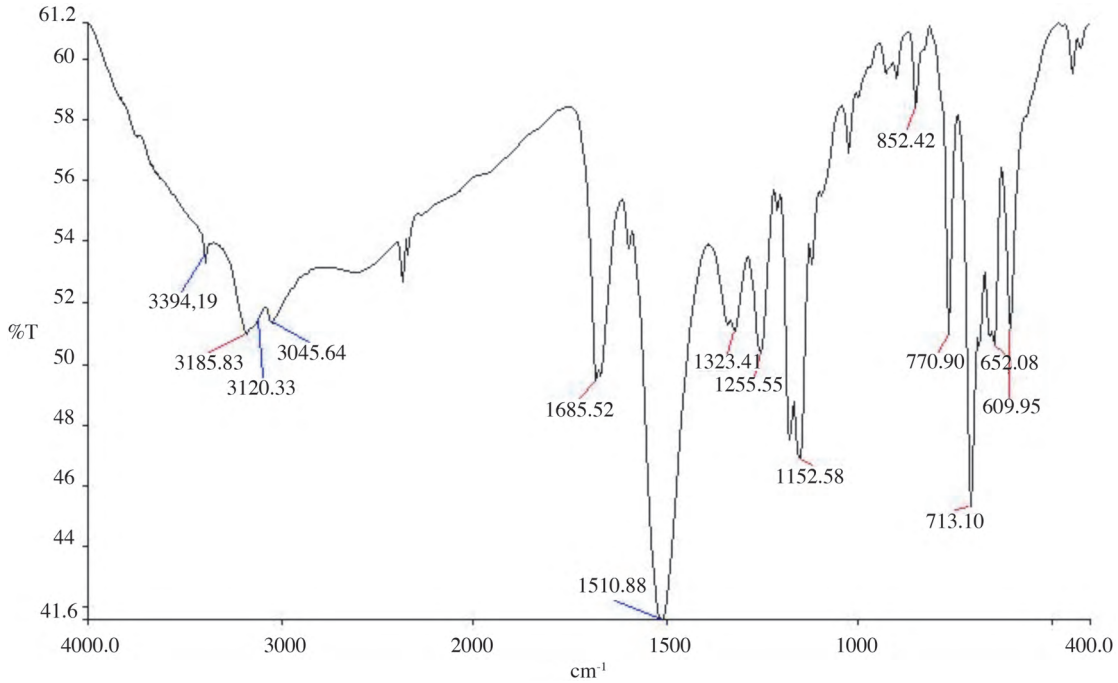


Figure 7. Infrared spectrum of 1,1'-(naphthalene-1,8-diyl)-3,3'-dibenzoyl-bisthiourea.

The molecule crystallized in the triclinic space group P-1. The molecule consists of 2 N-(carbamothioyl) benzamide groups bonded to 1,8 positions of the naphthalene molecule. These groups are in trans positions to each other. N-C bond distances are slightly different for these groups. While at the group of 1 position, N1-C11= 1.331 Å and C11-N2 = 1.393 Å, at 8 position these distances are N3-C19 = 1.316 Å and C19-N4 = 1.395 Å. This difference was probably due to intramolecular hydrogen bonding interaction forming a 6-member ring between the keto (C=O) group and the amine (–NH–) nitrogen. C-S bond distances reveal the character of the bonds as double bonds with 1.655 Å and 1.659 Å for C11-S1 and C19-S2, respectively. The geometry of the molecule moiety is stabilized by N—H···O type intramolecular hydrogen bonds with atoms N3—H33···O2 and N1—H11···O1. In the crystal structure, the molecules are linked by N4—H44···S2^{ii} [H44...S2= 2.61Å, N4—S2 = 3.454(2) Å and N4—H44...S2 = 167.4° with symmetry code (-x, -y, -z)] intermolecular hydrogen bonds to form centro symmetric dimers. This molecular interaction is consistent with similar related compounds.[12,13] Intermolecular hydrogen bonds also occur between with N1—H11···O1^{i} [H11...O1= 2.66 Å, N1—O1= 3.196(3) Å and N1—H11...O1= 122° with symmetry code (-x + 1, -y, -z)]. The crystal structure also has C-H...π stacking. This C-H...π interaction occurs between C14 atoms Cg1 (the centroid of the C1-C6 ring of naphthalene) and its symmetry equivalent at (1 – x, 2 – y, –z), with distances of H...Cg1 2.75 Å a centroid to centroid distance of 3.531(4) Å as seen in Table 3. The combinations of N—H···S bonds produce $R_2^2(8)$ rings.

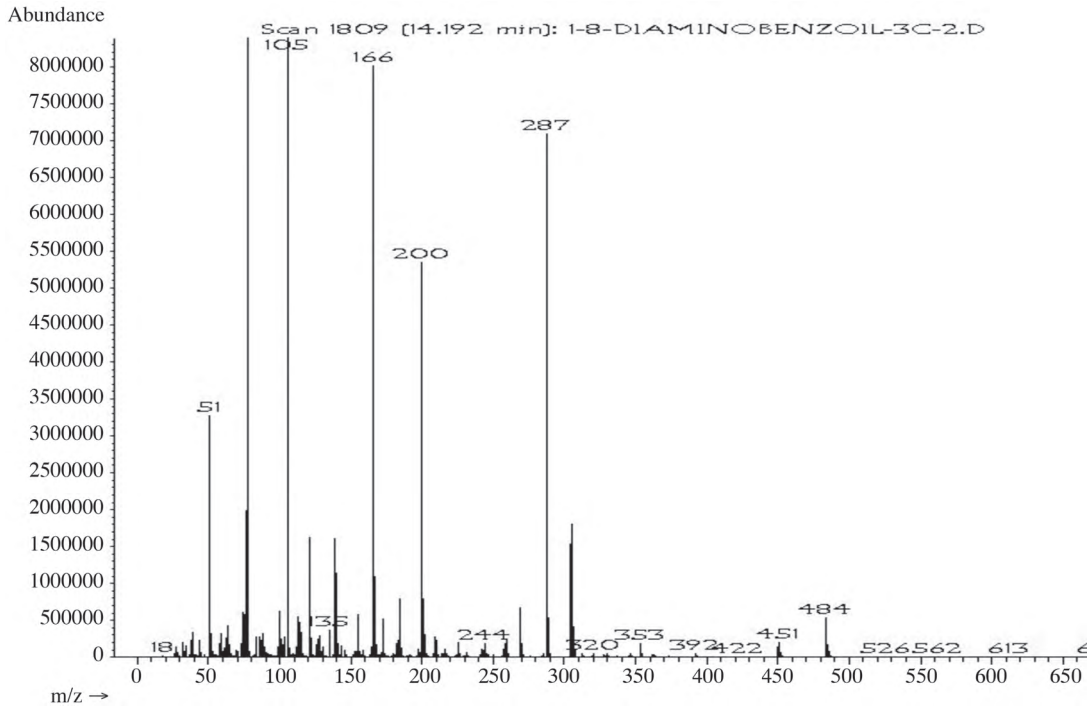


Figure 8. Mass spectrum of 1,1'-(naphthalene-1,8-diyl)-3,3'-dibenzoyl-bisthiourea.

Table 1. Crystal data and structure refinement for the title compound.

$C_{26}H_{20}N_4O_2S_2$	F(000) = 504
Mr = 484.58	Z = 2
Triclinic, P	Dx = 1.383 Mg m^{-3}
Hall symbol: -P 1	Melting point: 496 K
a = 8.1556 (8) Å	Mo Kα radiation, λ = 0.71073 Å
b = 12.0127 (11) Å	Cell parameters from 10540 reflections
c = 13.2081 (11) Å	$\theta = 1.7 - 27.2°$
α = 109.510 (7)°	μ = 0.26 mm^{-1}
β = 95.390 (7)°	T = 293 K
γ = 103.660 (7)°	Prism, colorless
V = 1163.92 (18) $Å^3$	0.51 × 0.38 × 0.21 mm
STOE IPDS 2 diffractometer	4555 independent reflections
Radiation source: sealed X-ray tube, 12 × 0.4 mm long-fine focus	1911 reflections with I > 2σ(I)
plane graphite	Rint = 0.119
Detector resolution: 6.67 pixels mm^{-1}	θ_{max} = 26.0°, θ_{min} = 1.7°
rotation method scans	h = -10 10
Absorption correction: integration X-RED32 (Stoe & Cie, 2002)	k = -14 14
Tmin = 0.926, Tmax = 0.973	l = -16 16
16,571 measured reflections	
Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix : Full	Hydrogen site location: inferred from neighboring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.041	H-atom parameters constrained
$wR(F^2)$ = 0.057	$w = 1/[\sigma^2(F_o^2) + (0.P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.69	$(\Delta/\sigma)_{max}$ = 0.002
4555 reflections	$\Delta\rho_{max}$ = 0.18 e $Å^{-3}$
307 parameters	$\Delta\rho_{min}$ = -0.20 e $Å^{-3}$

Table 2. Selected bond lengths (Å), bond angles (°), and torsion angles (°).

S2- C19	1.659 (3)	N2-C11	1.393 (3)	C10-N3-C19-N4	171.1 (1)
S1-C11	1.655 (3)	N1-C2	1.434 (3)	C10-N3-C19-S2	-10.2 (4)
C20-O2	1.226 (3)	C20-N4-C19	127.8 (1)	C20-N4-C19-N3	2.6 (4)
O1-C12	1.218 (3)	C2-C1-C10	127.5 (1)	C20-N4-C19-S2	-176.2
N1-C11	1.331 (3)	N1-C11-N2	115.3(3)	C11-N2-C12-O1	-9.3
N2-C12	1.384 (3)	C12-N2-C11	130.2(3)	C19-N4-C20-O2	0.5(2)

Table 3. Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···O1i	0.86	2.66	3.196 (3)	122
N3—H33···O2	0.86	1.95	2.631 (3)	135
N1—H11···O1	0.86	2.02	2.698 (3)	135
N4—H44···S2ii	0.86	2.61	3.454 (1)	167
Symmetry codes: (i) -x + 1, -y, -z; (ii) -x, -y, -z.				

Conclusions

We describe here a simple and easy way to prepare a bisthiourea-based receptor that allows naked-eye detection of fluoride ions among halide anions such as chloride, bromide, and iodine anions. The crystal structure of this compound revealed many significant structural phenomena, including inter- and intramolecular hydrogen bonds, and π-π interactions between phenyl and naphthyl groups, respectively. This compound, as a receptor, proves to be a colorimetric anion sensor that shows selective coloration for fluoride, hydroxide, and cyanide ions in DMSO solutions. This compound can be used as a potential chromogenic for these anion probes.

Supplementary material

Crystallographic data for the title compound have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 821335 for the structure reported in this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033.

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References

1. Schroeder, D. C. *Chem. Rev.*, **1995**, *50*, 185-228.
2. Xua, X.; Qianb, X.; Lia, Z.; Huang, Q.; Chena, G. *J. Fluorine Chem.* **2003**, *121*, 51-54.
3. Gamez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *Org. Biomol. Chem.* **2005**, *3,* 1495-1500.
4. a) Campo, R. D.; Criado, J. J.; Gheorghe, R.; Gonzalez, F. J.; Hermaso, M. R.; Sanz, F.; Manzano, J. L.; Monte, E.; Rodriguez-Fernandez, E. *J. Inorg. Biochem.* **2004**, *98*, 1307-1314; b) Weiqun, Z.; Yang, W.; Ligun, X.; Xianchen C. *J. Inorg. BioChem.* **2005**, *99*, 1314-1319.

5. Cunha, S.; Macedo, C.; Giselle, A. N. C.; Rodrigues, M. T.; Verde, R. B. V.; Nete, S. L. C.; Ivo, V. I.; Lariucci, C.; Sa, F. P. *Monatshefte für Chemie* **2007**, *138*, 511-516.
6. Saeed, A.; Khera, R. A.; Abbas, N.; Latif, M.; Sajid, I.; Füorke, U. *Turk. J. Chem.* **2010**, *34*, 335-345.
7. Merdivan, M.; Seyhan, S.; Gök, C. *Microchim. Acta* **2006**, *154*, 109-114.
8. Koch, K. R.; *Coord. Chem. Rev.* **2001**, *216-217*, 473-488.
9. Hu, J-H.; Wang, L-C.; Liu, H.; Wei, T-B. *Phosphorus, Sulfur and Silicon* **2006**, *181*, 2691-2698.
10. Thiam, E. I.; Diop, M.; Gaye, M.; Sall, A. S.; Barry, A. H. *Acta Cryst.* **2008**, E64: O776.
11. West, D. X.; Swearingen, J. K.; Hermetet, A. K.; Ackerman, L. J. *J. Mol. Struct.* **2001**, *562*, 95-105.
12. Aydin, F.; Unver, H.; Aykac, D.; Iskeleli, N. O. *J. Chem. Crystallogr.* **2010**, *40*, 1082-1086.
13. a) Suksai, C.; Pakawatchai, C.; Tuntulani, T. *J. Chem Crystallogr.* **2009**, *39*, 348-352; b) Kavak, G.; Ozbey, S.; Binzet, G.; Külcü, N. *Turk. J. Chem.* **2009**, *33*, 857-868.
14. Gale, P. A. *Chem. Commun.* **2011**, *47*, 82-86.
15. a) Estaban-Gomez, D.; Fabbirizzi, L.; Licchelli, M. *J. Org. Chem.* **2005**, *70*, 5717-5720; b) Hennrich, G.; Sonnenschein, H.; Resch-Genger, U. *Tetrahedron Lett.* **2001**, *42*, 2805-2808; c) Hutchins, R. S.; Molina, P.; Aiajarh, M.; Vidai, A.; Bachas, L. G. *J. Anal. Chem.* **1994**, *66*, 3188-3192.
16. Yamin, B. M.; Hassan, I. N. *Acta Cryst.* **2004**, *E60*: 2513-2514.
17. a) Sessler, J. L.; Gale, P. A.; Cho, W. S. *Anion Receptor Chemistry* Royal Society of Chemistry: Cambridge, UK, **2006**. b) Gale, P. A.; Sessler, J. L.; Kral, V.; Lynch, V. *J. Am. Chem. Soc.*, **1996**, *118*, 5140-5142.
18. Hutchins, R. S.; Molina, P.; Aiajarh, M.; Vidai, A.; Bachas, L. G. *J. Anal. Chem.* **1994**, *66*, 3188-3192.
19. a) Kang, S. O.; Begum, R. A.; Bowman-James, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 7882-7894; b) Kang, J.; Jang, S. P.; Kim, Y-H.; Lee, J. H.; Park, E. B.; Lee, H. G.; Kim, J. H.; Kim, Y.; Kim, S-J.; C. Kim, C. *Tetrahedron Lett.* **2010**, *51,* 6658-6662.
20. Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Let.*, **2004**, *6*, 3445-3448.
21. a) Hu, J. H.; Xu, L.; Wang, J.; Wei, T-B. *Phosphorus, Sulfur, and Silicon* **2008**, *183*, 1584-1591; b) Esteban-Gomez, D.; Fabbrizzi, L.; Licchelli, M. *J. Org. Chem.,* **2005**, *70*, 5717-5720; c) Amendola, V.; Esteban-Goamez, D.; Fabbrizzi, L.; Licchelli, M. *Acc. Chem. Res.*, **2006**, *39*, 343-353.
22. Zhang, Y.; Qin, J.; Lin, Q.; Wei, T. *J. Fluorine Chem.* **2006**, *127*, 1222-1227.
23. a) Chauhan, S. M. S. *Tetrahedron Letters* **2008**, *49*, 6646-6649; b) Morzherin, Y.; Rudkevich, D. M.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.*, **1993**, *58*, 7602-7605; c) Matthews, S. E.; Beer, P. D. *Supramolecular Chemistry*, **2005**, 17, 6, 411-435.
24. Mani, G.; Jana, D.; Kumar, R.; Ghorai, D. *Org. Lett.* **2010**, *12*, 3136-3139.
25. a) Upadhyay, K. K.; Kumar, A.; Mishra, R. K.; Fyles, T. P.; Upadhyay, S.; Thapliyal, K. *New J. Chem.* **2010**, *34*, 1862-1866; b) Shao, J.; Lin, H.; Yu, M.; Cai, Z.; Lin, H. *Talant,* **2008**, 551-555; c) Wang, Y. H.; Lin, H.; Lin, H. K. *Chin. J. Chem.* **2007**, *25*, 1430-1433; d) Qu, S.; Zhang, B.; Liao, H.; Bai, Z. *Chin. J. Inorg. Chem.* **2006**, *22*, 5, 817-822.
26. Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6,* 3445-3448.
27. Wang, Y.; Lin, H.; Shao, J.; Cai, Z-C.; Lin, H. K. *Talanta* **2008**, *74*, 1122-1125.
28. Lin, Z.; Ou, S.; Duan, C.; Zhang, B.; Bai, Z. *Chem. Commun.* **2006**, 624-626.

29. Estevez-Hernandez, O.; Otazo-Sanchez, E.; Hidalgo Cisneros, J. L.; Naranjo-Rodriguez, I.; Reguera, E. *Spectrochimica Acta Part A* **2005**, *62*, 964-971.

30. Arslan, H.; Florke, U.; Kulcu, N. *Turk. J. Chem.* **2004,** *28*, 673-678.

31. Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.,* **1993**, 97, 4552-4557.

32. Boiocchi, M.; Del Boca, L.; Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *J. Am. Chem. Soc.* **2004**, *126*, 16507-16514.

33. Stoe & Cie, X-AREA Version 1.18, Stoe & Cie, Darmstadt, Germany, **2002**.

34. Sheldrick, G. M.; SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, **1997**.

35. Farrugia, L. J. WinGX program for crystallography package. *J. Appl. Cryst.* **1999**, *32*, 837-838.

36. Sheldrick, G. M. SHELXL-97, Program for Crystal Structures Refinement, University of Göttingen, Germany, **1997**.

37. Stoe & Cie, X-RED32 Version 1.04, Stoe & Cie, Darmstadt, Germany, **2002**.