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-Supporting Information

Dansyl-Carbazole AIEE Material for Selective Recognition of Thiourea Derivatives

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General Information

All reagents were purchased from Sigma Aldrich and were used without further purification. THF and H_2O (buffered to pH 7.1) was used to perform analytical studies. All the fluorescence spectra were recorded on Agilent Technologies Cary Eclipse fluorescence spectrometer. UV-Vis spectra were recorded on Shimadzu UV-2450 spectrophotometer and FT-IR spectra were recorded on PerkinElmer FT-IR spectrometer (Spectrum Two, Serial No:88689). ^{1}H and ^{13}C NMR spectra were recorded on jeol 500 NMR spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Data are presented as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d= doublet, br = broad singlet, m = multiplet), coupling constant, *J* (Hz). TEM characterization was done by using FEI TECNAI G^2 20 –TWIN 200KV high resolution transmission electron microscopy (HRTEM). SEM characterization was done by using FEI-Nova nano SEM -450.

Preparation of HEPES Solution of pH = 7.1

To prepare 1 L HEPES buffer of 7.1 pH add 11.92 g of HEPES, 13.1 ml of 1M NaOH and 86.9 ml of 1 M NaCl and dilute it to 1L by adding distilled water. **R1**

R1- Buffers for pH and Metal Ion Control, D. Perrin, B. Dernpsey, John Wiley and Sons, New York, 1974.

Quantum yield

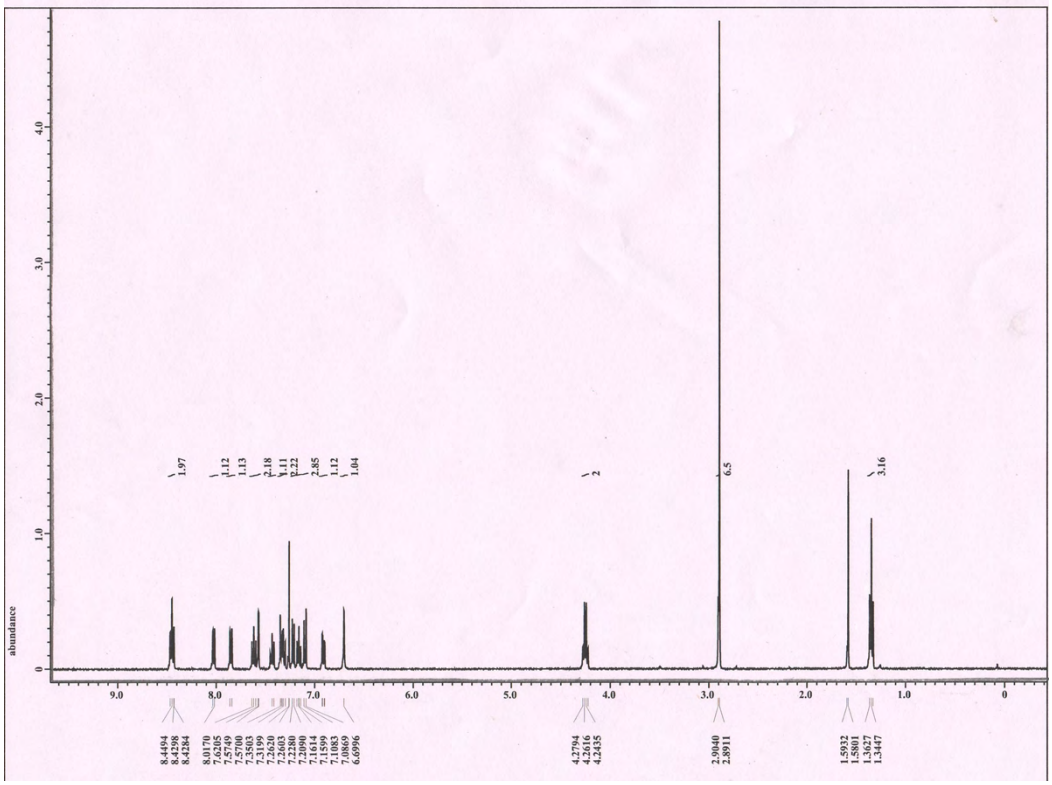
Experimental Procedure

Fluorescence quantum yield of **DACB** was determined at using quinine sulphate ($\Phi_{F(R)}$= 0.546) in 1N H_2SO_4 as standard. An excitation wavelength of 352 nm from a xenon spectroflurophotometer was used. The quantum yield was calculated by using equation (1), in which $\Phi_{F(S)}$ is the radiative quantum yield of sample, $\Phi_{F(R)}$ is the radiative quantum yield of reference, A_R and A_S are the absorbance of sample and the reference, respectively, F_R and F_S the area of emission for sample and the reference, respectively, n_R and n_S are the refractive indices of the sample and reference solutions.

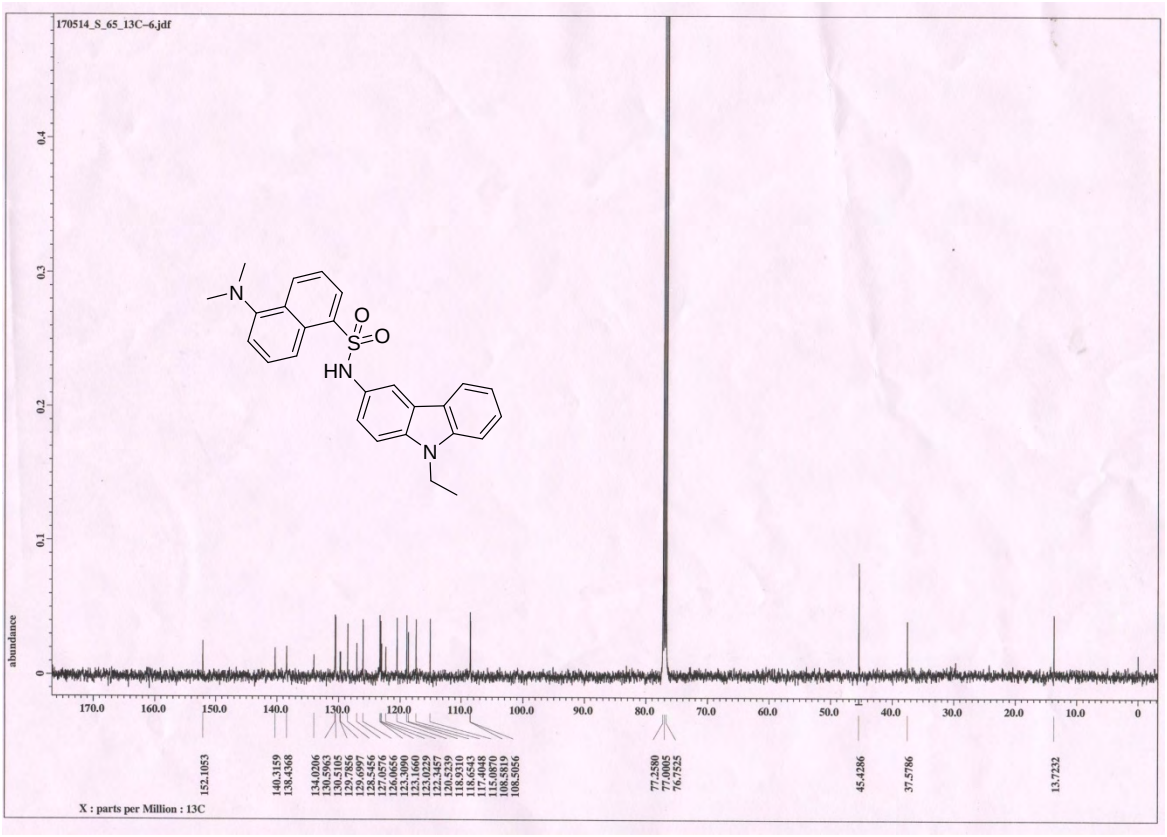
Equation 1

$$\Phi_{F(S)} = (A_R / A_S) (F_S / F_R) (n_S / n_R) \Phi_{F(R)}$$

^{1}H NMR SPECTRUM OF DACB



^{13}C NMR SPECTRUM OF DACB



MASS SPECTRUM OF DACB

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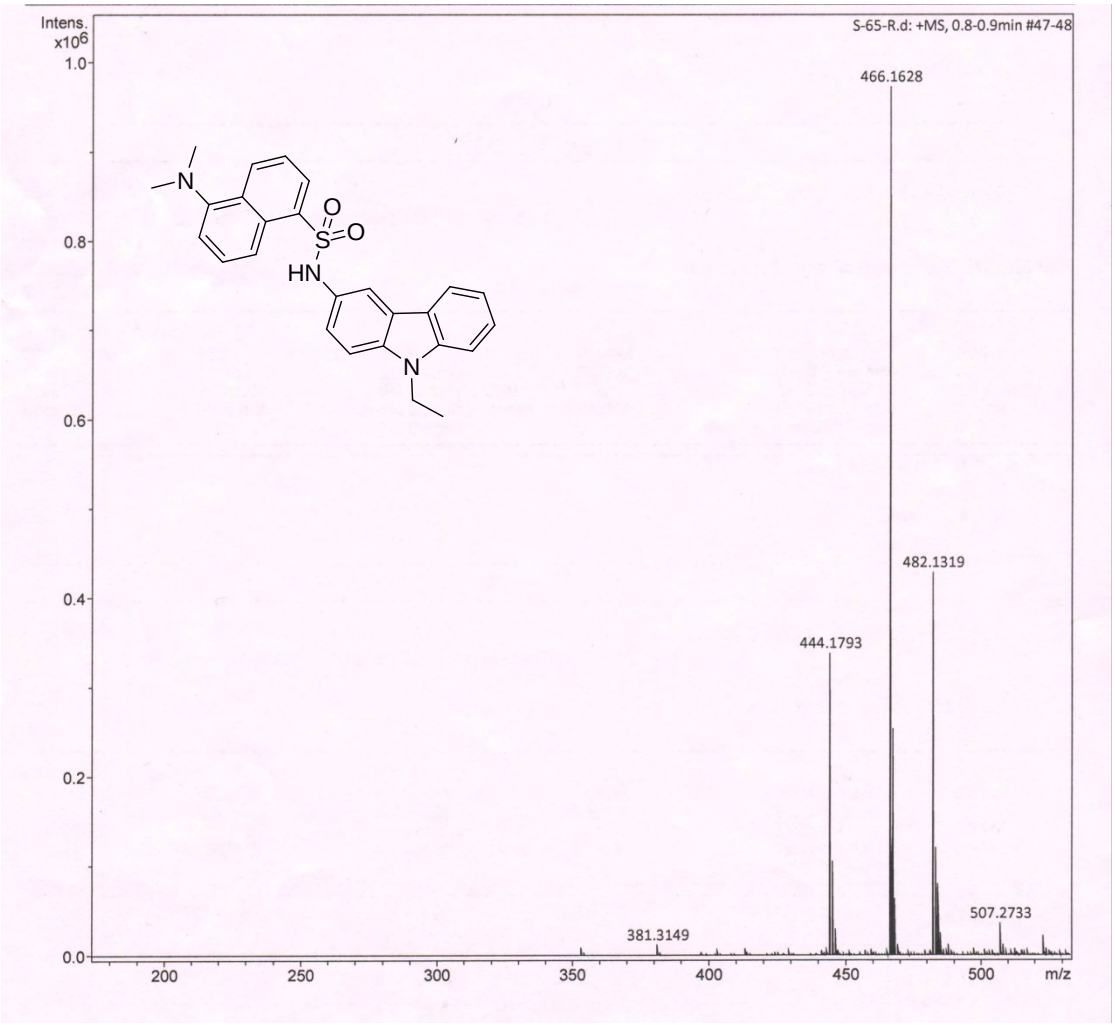
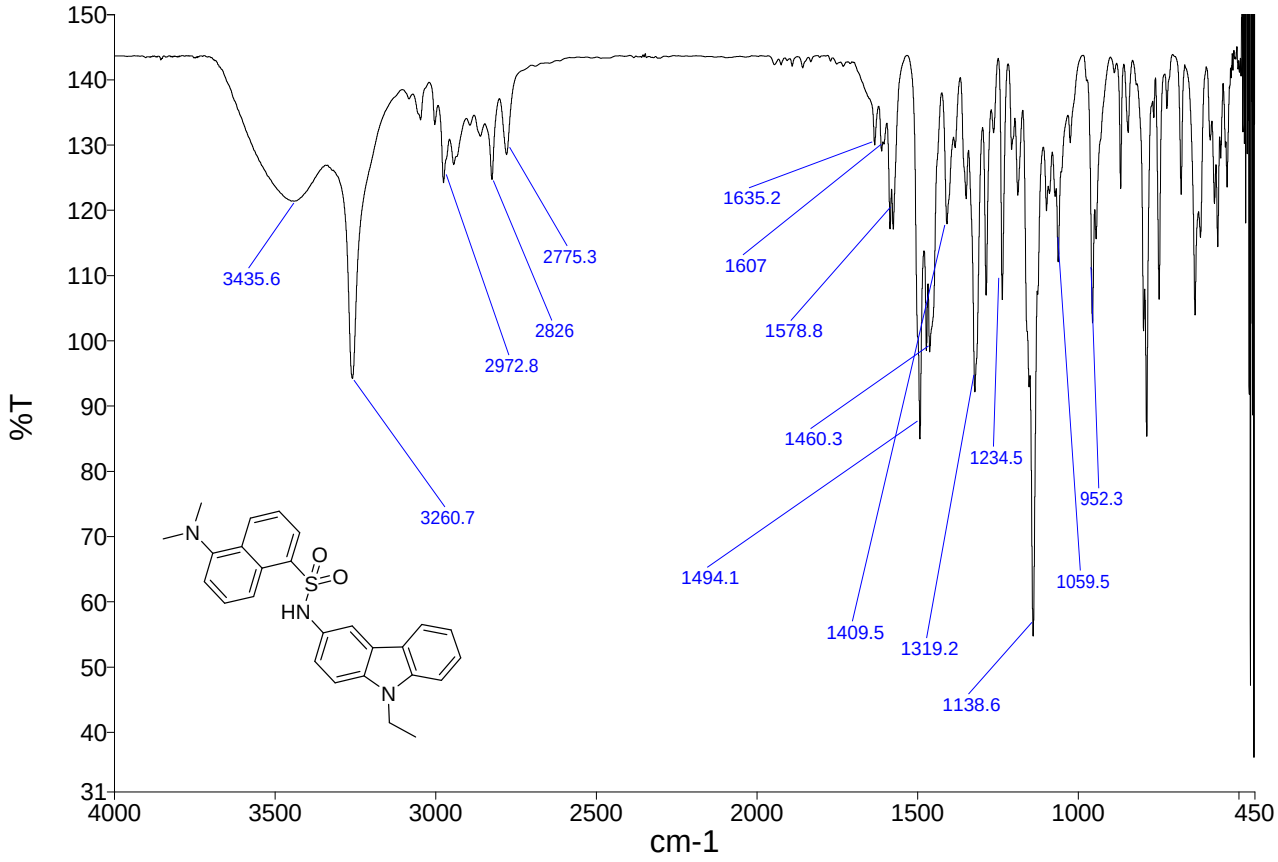


IR SPECTRUM OF DACB



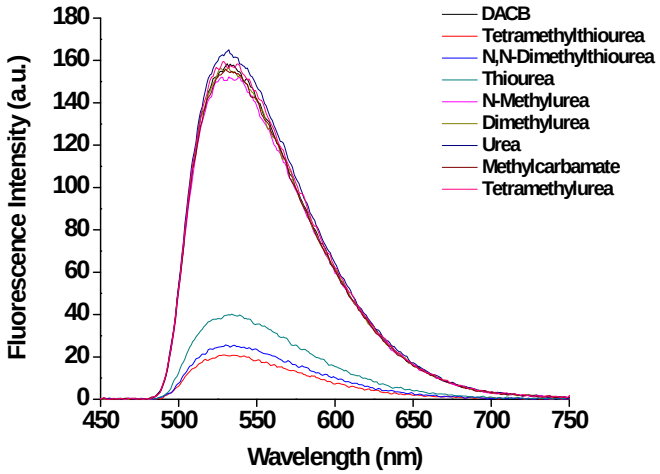


Fig 1. Fluorescence emission spectra of **DACB** (1.0 μM) in H_2O:THF (60:40, *v/v*) in presence of thioureas and ureas.

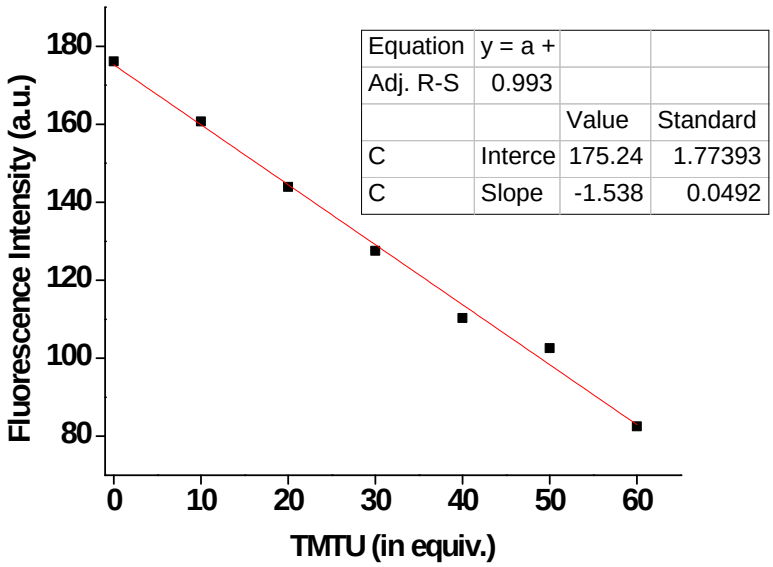


Fig 2. Detection limit of compound **DACB** showing the fluorescence intensity at 530 nm as a function of tetramethylthiourea concentration

S.no.	**DACB+analyte**	**σ**	**M**	**3 σ/M**	**Detection Limit**
1.	**DACB**+ Tetramethylthiourea	0.79	-1.538	1.54×10^{-6}	1.54μM

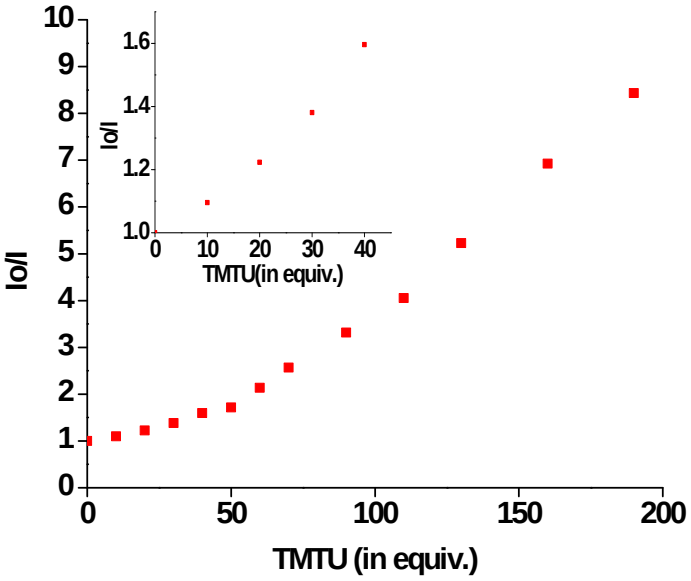


Fig. 3. Stern–Volmer plot of fluorescence response of **DACB** to tetramethylthiourea. Inset figure shows the Stern–Volmer plot obtained at lower concentration of tetramethylthiourea

X-ray crystallography

Single crystal X-ray data were collected with Agilent SuperNova, equipped with multilayer optics monochromated dual source (Cu and Mo) and Eos CCD detector, using Mo-Kα (0.71073 Å) radiation. Data acquisition and reduction were made using the program CrysAlisPRO.[R2] The structure was solved with ShelXS[R3] program and refined on F^2 by full matrix least-squares techniques with ShelXL[R3] program in Olex[2] (v.1.2) program package.[R4] Anisotropic displacement parameters were applied for all atoms, except hydrogen atoms. H atoms were calculated into their positions or located from the electron density map and refined as riding atoms using isotropic displacement parameters. The crystal and refinement data are summarized in Table 1. CCDC 1009952 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cifdata.

R2 : CrysAlisPro Program, version171.37.33c; Agilent Technologies:Oxford, 2012.

R3 : G. M. Sheldrick, *ActaCrystallogr*., 2008, **A 64**, 112.

R4 : O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. J. Puschmann, *Appl. Crystallogr*., 2009, **42**, 339.

Crystal data and structure refinement for **DACB**

Empirical formula	C26 H25 N3 O2 S
Formula weight	443.55
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P* 21/c
Unit cell dimensions	*a* = 15.635(5) Å
	b = 16.268(5) Å β = 103.891(5)°.
	c = 8.895(5) Å
Volume	2196.3(16) Å^3
Z	4
Density (calculated)	1.341 Mg/m^3
Absorption coefficient	0.177 mm^{-1}
F(000)	936
Theta range for data collection	1.835 to 25.650°.
Index ranges	-19<=h<=15, -19<=k<=17, -10<=l<=10
Reflections collected	20886
Independent reflections	4145 [R(int) = 0.0173]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4145 / 0 / 389
Goodness-of-fit on F^2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0773
R indices (all data)	R1 = 0.0326, wR2 = 0.0787
Extinction coefficient	n/a
Largest diff. peak and hole	0.290 and -0.366 e.Å^{-3}

Table 4. Bond lengths [Å] and angles [°] for test lt s 21.

S(1)-O(1)	1.4306(9)	N(3)-C(25)	1.4514(19)
S(1)-O(2)	1.4425(12)	C(3)-H(3)	0.956(17)
S(1)-N(2)	1.6248(11)	C(16)-C(17)	1.396(2)
S(1)-C(6)	1.7745(13)	C(16)-C(21)	1.4107(19)
N(1)-C(1)	1.4108(17)	C(16)-C(15)	1.4452(19)
N(1)-C(12)	1.4492(19)	C(13)-C(24)	1.4038(18)
N(1)-C(11)	1.458(2)	C(23)-C(22)	1.386(2)
C(8)-C(9)	1.3644(19)	C(23)-C(24)	1.387(2)
C(8)-C(7)	1.4059(19)	C(23)-H(23)	0.977(17)
C(8)-H(8)	0.960(16)	C(15)-C(22)	1.4101(19)
C(6)-C(7)	1.3729(18)	C(24)-H(24)	0.979(17)
C(6)-C(5)	1.4299(18)	C(17)-C(18)	1.386(2)
C(14)-C(13)	1.3813(19)	C(17)-H(17)	0.963(19)
C(14)-C(15)	1.3934(19)	C(7)-H(7)	0.968(15)
C(14)-H(14)	0.942(16)	C(11)-H(11C)	0.983(18)
C(9)-C(10)	1.4151(18)	C(11)-H(11B)	0.99(2)
C(9)-H(9)	0.956(16)	C(11)-H(11A)	0.98(2)
N(2)-C(13)	1.4302(16)	C(20)-C(19)	1.384(3)
N(2)-NH2	0.832(18)	C(20)-C(21)	1.395(2)
C(1)-C(2)	1.3722(19)	C(20)-H(20)	0.976(18)
C(1)-C(10)	1.4360(18)	C(18)-C(19)	1.395(3)
C(10)-C(5)	1.4291(17)	C(18)-H(18)	0.96(2)
C(12)-H(12C)	0.973(19)	C(26)-C(25)	1.504(3)
C(12)-H(12B)	0.995(19)	C(26)-H(26C)	0.99(2)
C(12)-H(12A)	0.980(19)	C(26)-H(26A)	1.02(2)
C(2)-C(3)	1.4071(19)	C(26)-H(26B)	0.95(3)
C(2)-H(2)	0.963(17)	C(19)-H(19)	0.99(2)
C(5)-C(4)	1.4163(17)	C(25)-H(25B)	0.98(2)
C(4)-C(3)	1.3673(19)	C(25)-H(25A)	1.02(2)
C(4)-H(4)	0.940(16)		
N(3)-C(21)	1.383(2)	O(1)-S(1)-O(2)	118.59(5)
N(3)-C(22)	1.3851(18)	O(1)-S(1)-N(2)	104.91(6)
		O(2)-S(1)-N(2)	108.09(6)

O(1)-S(1)-C(6)	110.03(6)	C(4)-C(5)-C(10)	118.87(11)
O(2)-S(1)-C(6)	105.66(5)	C(4)-C(5)-C(6)	124.26(11)
N(2)-S(1)-C(6)	109.36(6)	C(10)-C(5)-C(6)	116.84(10)
C(1)-N(1)-C(12)	116.57(12)	C(3)-C(4)-C(5)	120.07(12)
C(1)-N(1)-C(11)	115.75(11)	C(3)-C(4)-H(4)	119.7(9)
C(12)-N(1)-C(11)	111.51(11)	C(5)-C(4)-H(4)	120.2(9)
C(9)-C(8)-C(7)	120.02(12)	C(21)-N(3)-C(22)	108.41(11)
C(9)-C(8)-H(8)	120.1(9)	C(21)-N(3)-C(25)	126.30(13)
C(7)-C(8)-H(8)	119.8(9)	C(22)-N(3)-C(25)	124.94(13)
C(7)-C(6)-C(5)	121.86(11)	C(4)-C(3)-C(2)	121.40(12)
C(7)-C(6)-S(1)	115.99(9)	C(4)-C(3)-H(3)	119.9(10)
C(5)-C(6)-S(1)	122.03(9)	C(2)-C(3)-H(3)	118.7(10)
C(13)-C(14)-C(15)	118.79(12)	C(17)-C(16)-C(21)	120.02(13)
C(13)-C(14)-H(14)	120.3(10)	C(17)-C(16)-C(15)	133.58(13)
C(15)-C(14)-H(14)	120.9(10)	C(21)-C(16)-C(15)	106.40(12)
C(8)-C(9)-C(10)	121.29(12)	C(14)-C(13)-C(24)	121.22(12)
C(8)-C(9)-H(9)	121.3(9)	C(14)-C(13)-N(2)	117.51(11)
C(10)-C(9)-H(9)	117.3(9)	C(24)-C(13)-N(2)	121.22(12)
C(13)-N(2)-S(1)	125.60(9)	C(22)-C(23)-C(24)	118.69(13)
C(13)-N(2)-NH2	115.2(11)	C(22)-C(23)-H(23)	122.1(10)
S(1)-N(2)-NH2	111.1(11)	C(24)-C(23)-H(23)	119.2(10)
C(2)-C(1)-N(1)	123.15(12)	C(14)-C(15)-C(22)	119.81(12)
C(2)-C(1)-C(10)	119.11(12)	C(14)-C(15)-C(16)	133.62(12)
N(1)-C(1)-C(10)	117.67(11)	C(22)-C(15)-C(16)	106.56(12)
C(9)-C(10)-C(5)	119.56(11)	C(23)-C(24)-C(13)	120.31(13)
C(9)-C(10)-C(1)	120.84(11)	C(23)-C(24)-H(24)	120.5(10)
C(5)-C(10)-C(1)	119.51(11)	C(13)-C(24)-H(24)	119.2(10)
N(1)-C(12)-H(12C)	112.9(11)	N(3)-C(22)-C(23)	129.67(13)
N(1)-C(12)-H(12B)	109.4(10)	N(3)-C(22)-C(15)	109.22(12)
H(12C)-C(12)-H(12B)	110.2(15)	C(23)-C(22)-C(15)	121.10(13)
N(1)-C(12)-H(12A)	107.5(11)	C(18)-C(17)-C(16)	118.58(15)
H(12C)-C(12)-H(12A)	106.9(15)	C(18)-C(17)-H(17)	121.7(11)
H(12B)-C(12)-H(12A)	109.8(15)	C(16)-C(17)-H(17)	119.7(11)
C(1)-C(2)-C(3)	120.82(12)	C(6)-C(7)-C(8)	120.06(12)
C(1)-C(2)-H(2)	118.8(10)	C(6)-C(7)-H(7)	119.0(9)
C(3)-C(2)-H(2)	120.4(10)	C(8)-C(7)-H(7)	120.9(9)

N(1)-C(11)-H(11C)	113.0(10)	H(26C)-C(26)-H(26A)	110.0(18)
N(1)-C(11)-H(11B)	111.8(11)	C(25)-C(26)-H(26B)	108.5(15)
H(11C)-C(11)-H(11B)	105.6(15)	H(26C)-C(26)-H(26B)	105(2)
N(1)-C(11)-H(11A)	108.1(11)	H(26A)-C(26)-H(26B)	110.9(19)
H(11C)-C(11)-H(11A)	108.7(15)	C(20)-C(19)-C(18)	122.05(15)
H(11B)-C(11)-H(11A)	109.5(15)	C(20)-C(19)-H(19)	119.0(12)
C(19)-C(20)-C(21)	117.33(15)	C(18)-C(19)-H(19)	118.9(12)
C(19)-C(20)-H(20)	120.7(11)	N(3)-C(25)-C(26)	112.35(16)
C(21)-C(20)-H(20)	121.9(11)	N(3)-C(25)-H(25B)	108.1(12)
N(3)-C(21)-C(20)	129.26(14)	C(26)-C(25)-H(25B)	109.7(12)
N(3)-C(21)-C(16)	109.37(12)	N(3)-C(25)-H(25A)	108.0(12)
C(20)-C(21)-C(16)	121.37(14)	C(26)-C(25)-H(25A)	110.0(12)
C(17)-C(18)-C(19)	120.63(16)	H(25B)-C(25)-H(25A)	108.6(17)
C(17)-C(18)-H(18)	118.6(12)		
C(19)-C(18)-H(18)	120.7(12)		
C(25)-C(26)-H(26C)	112.3(13)		
C(25)-C(26)-H(26A)	109.8(13)		

Symmetry transformations used to generate equivalent atoms:

Table 9. Hydrogen bonds for test lt s 21 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(24)-H(24)...O(2)	0.979(17)	2.485(16)	3.1670(19)	126.5(12)
N(2)-NH2...O(2)#1	0.832(18)	2.112(18)	2.9417(17)	175.0(16)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z+1/2