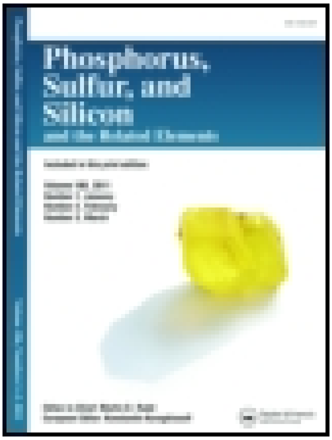

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Synthesis and Crystal Structure of N , N ′ -(p -phenyl)-bis-(p-nitro)benzoylthiourea

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Synthesis and Crystal Structure of *N,N′*-(*p*-phenyl)-bis-(p-nitro)benzoylthiourea

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N, N′-(p-phenyl)-bis-(p-nitro)benzoylthiourea was synthesized and characterized by elemental analysis as well as IR and ^1H NMR spectroscopy. The crystal structure of the title compound was determined by single crystal X-ray diffraction. It was crystallized in triclinic space group of P-1, a = 8.1084(12), b = 11.9185(13), c = 12.6061(15) Å, α = 62.213(2)°, β = 71.266(2)°, γ = 88.014(3)°, Z = 1, V = 1011.0(2)Å^3. The intramolecular N-H· · ·O hydrogen bonding interactions between the N-H and the oxygen atom of C=O groups suport N, N′-(p-phenyl)-bis-(p-nitro)benzoylthiourea framework. the solvent DMF molecules are accommodated in the framework by intermolecular N-H··O hydrogen bonds between N-H and the oxygen atom of DMF in the title compound, which help to assemble into supramolecular structure.

Keywords Crystal structure; *N, N′*-(*p*-phenyl)-bis-(*p*-nitro)benzoylthiourea; Synthesis; X-ray diffraction

INTRODUCTION

The extensive applications of thiourea derivatives are paid much attention. Besides their good biological activities,[1–3] some thioureas have good inhibition effect on the corrosion of mild steel in hydrochloric acid medium and they are excellent neutral ion carrier,[4,5] which are also applied in the extraction of trace metals and the separation of platinum group metal and in the a coordination reaction etc.[6–8] The existence of carbonyl and sulphur carbonyl groups in benzoylthiourea enhances the coordination ability.

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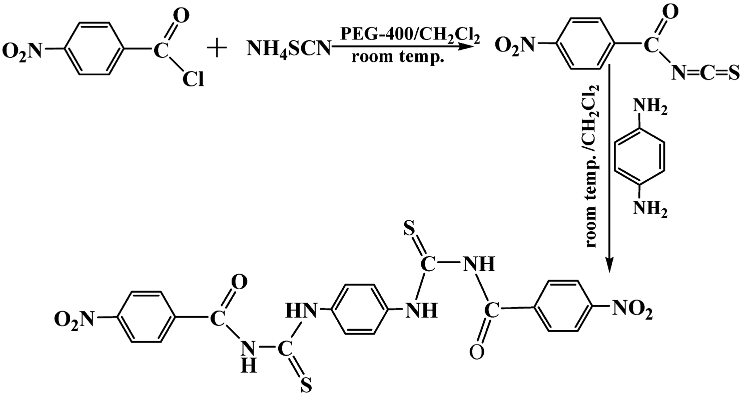
Studies of a number of substituted thioureas including N-benzoyl-N′-thiourea indicate an intramolecular hydrogen bond between NH group and oxygen atom,[9,10] which help to assemble into supramolecular structure.[11,12] Here, in continuation of our previous studies on synthesis and structural characterization of *N*-(*o*-Chloro)benzoyl-*N*′-(3-pyridyl)thiourea,[13] a novel bis-benzoylthioureas,*N*,*N*′-(*p*-phenyl)-bis-(*p*-nitro)benzoylthiourea *N*,*N*′-dimethylformamide disolvate has been synthesized (Scheme 1) and structurally characterized by X-ray crystallography.



SCHEME 1 Synthetic route to *N*,*N*′-(*p*-phenyl)-bis-(*p*-nitro)benzoylthiourea.

RESULTS AND DISCUSSION

The title compound has been synthesized and characterized by elemental analysis, IR as well as ^{1}H NMR spectroscopy and single crystal X-ray diffraction analysis. The IR data of the title compound show two ν_{N-H} stretching bands at 3341 and 3191 cm^{-1}. The C=O groups stretching bands appears at 1675 cm^{-1}. A strong band at 1152 cm^{-1} is observed for the title compound and is assigned to $\nu_{C=S}$ stretching vibration.

The ^{1}H NMR data of the title compound show that the chemical shifts of hydrogen on nitrogen appear in the low field, which chemical shifts are with 11.98 and 12.42 ppm. The chemical shifts (8.052, 8.187, 8.338 ppm) of hydrogen atoms on the benzene rings are in a lower field than the average chemical shift (7.270 ppm) of hydrogen atoms on the non-substituted benzene ring, which due to the substituted groups NO_2 and C=O of the benzene ring.

The crystal data and parameters relevant to the structure determination and refinement for the title compound are listed in Table I; selected bond lengths and bond angles and hydrogen bonds parameters are listed in Table II and Table III. The molecular structure in the

TABLE I Crystal Data and Structure Refinement for the Title Compound

Formula	$C_{34}H_{48}N_{10}O_{10}S_2$	V/Å^3	1011.0(2)
Mr	820.94	Z	1
Crystal system/ Space group	Triclinic/ P-1	Dr/(mg·m^{-3})	1.348
a/Å	8.1084(1)	λ/Å	0. 71073
b/Å	11.9185(1)	θ range/°	1.95–25.00
c/Å	12.6061(2)	μ/cm^{-1}	1.98
α/°	62.213(2)	T/K	298(2)
β/°	71.266(2)	Block, Yellow	
γ/°	88.014(3)	Crystal size	0.53 × 0.41 × 0.28 mm
Data collection			
Bruker SMART diffractometer	R(int) = 0.0482		
ϕ/ω scans	$\theta_{\max} = 25.00$		
5258 measured reflections	$-9 \leq h \leq 8$		
3499 independent reflections	$-14 \leq k \leq 14$		
2056 reflections with $I > 2\delta(\mathrm{I})$	$-14 \leq l \leq 14$		
Refinement			
Refinement on F^2		253 parameters	
$R\,[F^2 > 2\sigma(F^2)] = 0.064$		$\omega = 1/[\sigma^2(F_o^2) + (0.0925P)^2 + 0.1348P]$	
$\omega R(F^2) = 0.161$		Where $P = (F_o^2 + 2F_c^2)/3$	
S = 1.014		$\Delta\rho_{\max} = 0.317$ e Å^{-3}	
3499 reflections		$\Delta\rho_{\min} = -0.317$ e Å^{-3}	

crystal with atom labelling and a view of packing diagram along the a-axis, resulting from intermolecular hydrogen bonding are shown in Figure 1 and Figure 2, respectively.

A yellow block-shaped crystal of the title compound with approximate dimensions of 0.53 × 0.41 × 0.28 mm was mounted on a Bruker Smart diffractometer equipped with an Apex CCD area detector. Intensity data were collected using a graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 298 (2) K. The structure was solved by Direct Methods (SHELXS 97) [14] and refined by full matrix least squares on F^2 using the program SHELXL 97.[15] All hydrogen atoms were calculated. Hydrogens on nitrogens were located by difference Fourier maps, placed at N–H = 0.8600 Å and refined isotropically. Hydrogens attached to carbons were located in their calculated positions (C–H = 0.9300 Å), assigned fixed thermal parameters of $U_{\mathrm{iso}} = 0.05$ Å^2 and refined using

TABLE II Selected Bond Lengths [Å] and Bond Angles [°] for the Title Compound

Bond	Dist.	Bond	Dist.	Bond	Dist.
N(1)-C(1)	1.330(4)	C(2)-C(4)	1.373(5)	C(10)-C(11)	1.375(5)
N(1)-C(2)	1.406(4)	C(2)-C(3)	1.392(5)	N(4)-C(12)	1.301(5)
N(2)-C(5)	1.367(4)	C(3)-C(4)	1.379(5)	N(4)-C(13)	1.440(6)
N(2)-C(1)	1.400(4)	C(5)-C(6)	1.494(5)	N(4)-C(14)	1.450(5)
N(3)-O(2)	1.212(4)	C(6)-C(7)	1.377(5)	N(5)-C(15)	1.311(7)
N(3)-O(3)	1.222(4)	C(6)-C(11)	1.387(4)	N(5)-C(16)	1.388(6)
N(3)-C(9)	1.475(4)	C(7)-C(8)	1.375(5)	N(5)-C(17)	1.479(7)
O(1)-C(5)	1.216(4)	C(8)-C(9)	1.376(5)	O(4)-C(12)	1.221(4)
S(1)-C(1)	1.651(4)	C(9)-C(10)	1.367(5)	O(5)-C(15)	1.212(8)
Bond angles	Deg.	Bond angles	Deg.	Bond angles	Deg.
C(1)-N(1)-C(2)	131.7(3)	N(1)-C(1)-N(2)	114.2(3)	N(2)-C(5)-C(6)	116.5(3)
C(5)-N(2)-C(1)	127.6(3)	N(1)-C(1)-S(1)	127.7(3)	C(7)-C(6)-C(11)	119.8(3)
O(2)-N(3)-O(3)	123.2(3)	N(2)-C(1)-S(1)	114.2(3)	C(7)-C(6)-C(5)	122.9(3)
O(2)-N(3)-C(9)	118.2(3)	N(2)-C(1)-S(1)	118.1(3)	C(11)-C(6)-C(5)	117.1(3)
O(3)-N(3)-C(9)	118.6(3)	C(4)-C(2)-C(3)	118.7(3)	C(8)-C(7)-C(6)	120.9(3)
C(12)-N(4)-C(13)	120.5(4)	C(4)-C(2)-N(1)	125.4(3)	C(7)-C(8)-C(9)	117.7(3)
C(12)-N(4)-C(14)	121.8(4)	C(3)-C(2)-N(1)	115.8(3)	C(10)-C(9)-C(8)	123.0(3)
C(13)-N(4)-C(14)	117.7(4)	C(4)#1-C(3)-C(2)	121.2(3)	C(12)-C(11)-C(10)	118.6(2)
C(15)-N(5)-C(16)	125.6(6)	C(2)-C(4)-C(3)#1	120.1(3)	C(10)-C(9)-N(3)	118.8(3)
C(15)-N(5)-C(17)	119.2(5)	O(1)-C(5)-N(2)	123.8(3)	C(8)-C(9)-N(3)	118.2(3)
C(16)-N(5)-C(17)	115.2(5)	O(1)-C(5)-C(6)	119.7(3)	O(5)-C(15)-N(5)	123.9(7)
C(9)-C(10)-C(11)	118.5(3)	C(10)-C(11)-C(6)	120.1(3)	O(4)-C(12)-N(4)	125.4(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z.

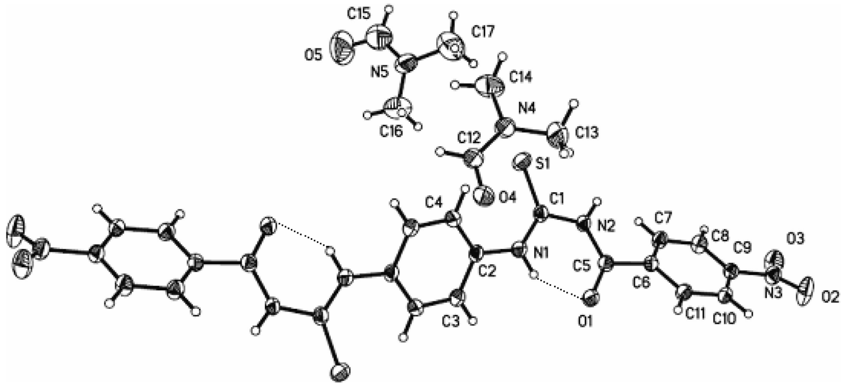
a riding model. The final refinements converged at $R_1 = 0.0645$, $wR_2 = 0.1607$ with $\omega = 1 / [\sigma^2(F_o^2) + (0.0925P)^2 + 0.1348P]$, where $P = (F_o^2 + 2F_c^2) / 3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The largest differential peak and hole were 0.317 and -0.317 e Å^{-3}. The structural plots were drawn with SHELXL 97 software package.

The X-ray crystallographic analysis of the title compound revealed the carbonyl and thiocarbonyl moieties point in approximately opposite

TABLE III Hydrogen Bonds Parameters for the Title Compound

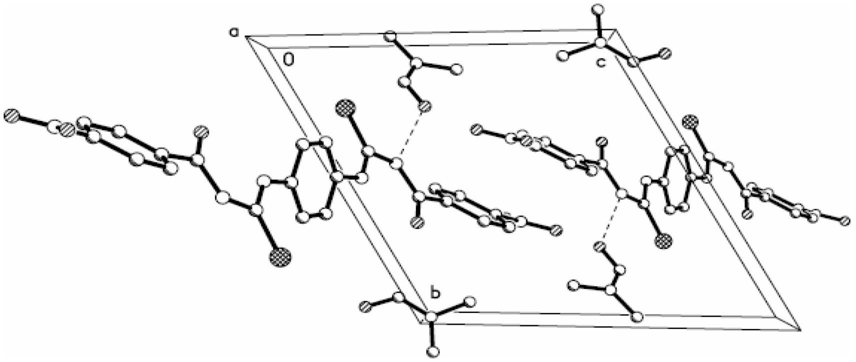
D-H···A	D-H	H···A	D···A	∠D-H···A
N(1)-H(1N)···O(1)	0.86(2)	1.867(2)	2.602(3)	142.37(2)
N(2)-H(2N)···O(4)*	0.86(2)	2.006(2)	2.821(3)	157.73(2)

Symmetry transformations used to generate equivalent atoms: *: x-1, y, z.



SCHEME 2 Molecular structure in the crystal with atom numbering of the title compound. Intramolecular H-bonds are indicated by dashed lines.

directions, there is intramolecular hydrogen bonding N1-H1···O1 (d(H1···O1) = 1.867(2) Å; d(N1···O1) = 2.602(3) Å; ∠N1-H1···O1 = 142.37°) between the carbonyl group and the N1-H1 group, the six atoms (C5/N2/C1/N1/H1/O1) in the hydrogen-bonded ring almost coplanar, the torsion angles of C(5)-N(2)-C(1)-N(1) and C(1)-N(2)-C(5)-O(1) are −3.8(5)° and 1.4(6)°, respectively. The formtion of coplanar hydrogen-bonded ring promotes the stability of the thiourea compounds, which is difficult for the oxygen atom on carbonyl of benzoylthioureas to particpate in the coordination with metal ions.[16,17] The C=O bond length is 1.216(4) Å, longer than the average C=O bond length (1.200 Å), which is due to intramolecular hydrogen bonding



SCHEME 3 View of packing diagram along the a-axis in the crystal structure of the title compound. Intermolecular H-bond are indicated by dashed lines.

interactions. There are two *N*,*N*′-dimethylformamide molecules in the structure of *N*,*N*′-(*p*-phenyl)-bis-(*p*-nitro)benzoylthiourea.

A view of the inter-molecular hydrogen bond in a packing diagram along a-axis in the crystal lattice of the title compound shows it contains a molecule in a crystal packing. There are intermolecular hydrogen bondings N2-H2···O4(x-1, y, z) (d(H2···O4) = 2.006(2) Å; d(N2···O4) = 2.821(3) Å; ∠N1-H1···O1 = 157.73°) between the carbonyl group of *N*,*N*′-dimethylformamide and the N2-H2 group. There are π-π interactions between two benzene rings of neighboring molecules in the crystal packing along a-axis and the distance between two benzene rings planes is 1.132(3) Å.

The crystal structure shows that thioureas are good donors of hydrogen bondings, which may form inter- and intramolecular hydrogen bondings, and the intermolecular hydrogen bonding assembled into supramolecule. There are the π-π interaction between the aromatic rings, which help to assemble into supramolecular structure.[11,12]

EXPERIMENTAL

All chemicals were of analytical reagent grade and were used without further purification. C, H, and N analyses were obtained using a VarioEL V3.00 automatic elemental analysis instrument. The IR spectra in the range of 400–4000 cm^{-1} were recorded with a VERTEX70 FT-IR spectrophotometer using KBr pellets. ^1H NMR spectra were obtained with a German Bruker AVANCE DRX-400 spectrometer. The single crystal structure determination by X-ray diffraction was performed with a Bruker Smart diffractometer equipped with an APEX CCD area detector. Melting points were obtained using a X4 microscopic melting point apparatus (Beijing Taike Instrument) and are uncorrected.

Synthesis

(*p*-Nitro)benzoyl chloride (1.86 g, 10 mmol) was reacted with ammonium thiocyanate (1.14 g, 15 mmol) in CH_2Cl_2(25 ml) solution under soild-liquid phase transfer catalysis, using polyethylene glycol-400 (0.18 g) as the catalyst, to give the corresponding (*p*-nitro)benzoyl isothiocyanate under stirring at the room temperature, followed by slow addition of 15 ml CH_2Cl_2 solution dissolved p-phenylenediamine (1.60 g, 0.01 mmol). The corresponding yellow compound precipitated immediately. The product was filtered, washed with water and CH_2Cl_2, dried, and recrystallized from THF to give the title compound (*N*,*N*′-(*p*-phenyl)-bis-(*p*-nitro)benzoylthiourea). Yield: 72.6%. m.p. 243–244°.

Elemental analysis – found: C, 50.38%; H, 3.07%; N, 16.02%; calcd. for $C_{34}H_{48}N_{10}O_{10}S_2$: C, 50.27%; H, 3.15%; N, 15.99%. Selected IR data (cm^{-1}, KBr pellet): 3341, 3191 (ν_{NH}), 1675 ($\nu_{C=O}$), 1152 ($\nu_{C=S}$).^{1}H NMR (400 MHz, DMSO-d$_6$, δ, ppm): 8.052 (d, $J = 17.2$ Hz, 4H, ArH), 8.187 (d, $J = 8.2$ Hz, 4H, ArH), 8.338 (dd, $J = 17.2$, 7.2 Hz, 4H, ArH), 11.98 (s, 2H, NH), 12.42 (s, 2H, NH).

A DMF solution of the title compound was placed in a diethyl ether atmosphere, after several days, along with diffusion of diethyl ether into the DMF solution of the title compound, yellow block-shaped single crystal suitable for X-ray crystallographic analysis were obtained.

Further details of the crystal structure investigation may be obtained from the the Cambridge Crystallographic Data Centre, Postal Address: CCDC, 12 Union Road, CAMBRIDGE CB2 1EZ, UK. Telephone: (44) 01223 762910 Fax: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk on quoting the depository number CCDC 652645.

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