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Theoretical and experimental studies on *N*-(6-methylpyridin-2-yl-carbamothioyl)biphenyl-4-carboxamide

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ABSTRACT

A novel thiourea derivative, *N*-(6-methylpyridin-2-yl-carbamothioyl)biphenyl-4-carbox amide, is synthesized and characterized by elemental analysis, FT-IR, NMR and single crystal X-ray diffraction study. There are two independent molecules A and B in the asymmetric unit. The short bond lengths of the C-N bonds in the central thiourea fragment indicate partial double bond character in this fragment of the title compound. These results can be explained by the existence of resonance in this part of the molecule. Each A and B molecule is stabilized with an intramolecular N-H•••O hydrogen bond which results in the formation of a pseudo six membered ring. In addition, the independent molecules are linked into a chain along the *c* axis by weak N-H•••S intermolecular hydrogen bonds. The conformational behavior and structural stability of the optimized geometry of the title compound were also investigated by utilizing ab- initio calculations with 6-31G* basis set at HF, BLYP, and B3LYP levels. The calculated parameters are in good agreement with the corresponding X-ray diffraction values.

1. Introduction

Very flexible thiourea derivatives are able to coordinate to transition metal atoms as neutral ligands, monoanions or dianions [1-10]. The oxygen, nitrogen and sulfur donor atoms in thiourea derivatives provide a multitude of bonding possibilities. The coordination chemistry of substituted thiourea derivatives has led to some practical applications such as liquid-liquid extraction, pre-concentration and highly efficient chromatographic separations [9-10].

Our team has been focusing on the synthesis, characterization, crystal structure, thermal behavior and antimicrobial activity of new thiourea derivatives [1-8,11-24]. Based upon the literature search and to the best of our knowledge, there is no report on the synthesis and characterization of the title compound.

In this article, we report the preparation and characterization of a novel thiourea compound, *N*-(6-methyl pyridin-2-yl-carbamothioyl)biphenyl-4-carbox amide and its crystal structure. In addition, we have calculated the conformational behavior and structural stability of the optimized geometry of the title compound in the ground state by using the Hartree–Fock (HF) [25], density functional using Becke's three-parameter hybrid functional [26] with the Lee, Yang, and Parr correlation functional methods (B3LYP) [27], Becke's exchange functional in combination with the Lee, Yang and Parr correlation functional methods (BLYP) [26,27].

2. Experimental

2.1. Synthesis

The compound was prepared with a procedure similar to that reported in the literature [2,4]. A solution of biphenyl-4-carbonyl chloride (0.01 mol) in acetone (50 cm^3) was added dropwise to a suspension of potassium thiocyanate (0.01 mol) in acetone (30 cm^3). The reaction mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of 6-methylpyridin-2-amine (0.01 mol) in acetone (10 cm^3) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 300 cm^3) was added to the solution to acidify it, which was then filtered. The solid product was washed with water and purifed by recrystalization from an ethanol: dichloro methane mixture (1:2). *N*-(6-methylpyridin-2-yl-carbamothioyl) biphenyl-4-carboxamide: White. Yield: 93 %. M.p.: 170-172 $^{\circ}$C. Anal. Calcd. for $C_{20}H_{17}N_3OS$: C, 69.1; H, 4.9; N, 12.1. Found: C, 69.2; H, 4.8; N, 12.2%. FT-IR (cm^{-1}): ν(NH) 3326 (w), 3218 (vw); ν(CH) 3025, 2917, 2846 (w); ν(CO) 1670 (s). ^{1}H-NMR (400 MHz, $CDCl_3$): 13.06 (s, 1H, CSN*H)*, 9.12 (s, 1H, CON*H*), 8.62 (d, 1H, Py), 8.00 (d, 2H, Bp), 7.77 (d, 2H, Bp), 7.68-7.64 (m, 3H, Bp, Py), 7.54-7.42 (m, 3H, Bp), 7.05 (d, 1H, Py), 2.55 (s, 3H, C*H$_3$*).

2.2. Instrumentation

C, H and N analyses were carried out on a Carlo Erba MOD 1106 elemental analyzer. ^{1}H-NMR spectra were obtained with a Bruker DPX-400 spectrometer using $CDCl_3$ as the solvent and

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TMS as an internal standard. Fourier transformation infrared (FT-IR) spectra were recorded in KBr pellets using a WinFirst Satellite FTIR spectrometer. The melting point was determined on a digital melting point instrument (Electrothermal model 9200). Single crystal X-ray data were collected on a Bruker AXS SMART APEX CCD diffractometer [28] using monochromated MoK$_\alpha$ radiation. The structure was solved [28,29] by direct and conventional Fourier methods. Full-matrix least-squares refinement [28,29] based on F^2. All apart from hydrogen atoms were refined anisotropically; hydrogen atoms were located from difference Fourier maps and refined at idealized positions with a 'riding model' and U(H) = 1.2 U(C$_{iso}$) and 1.5 U(C$_{iso}$) for methyl group, respectively. Further details concerning data collection and refinement are given in Table 1.

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

Empirical formula	$C_{20}H_{17}N_3OS$
Formula weight	347.43
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 11.266(2) Å
	b = 22.714(4) Å
	c = 13.603(2) Å
	β= 99.773(4)°
Volume	3430.7(11) Å^3
Z	8
Density (calculated)	1.345 Mg/m^3
Absorption coefficient	0.201 mm^{-1}
F(000)	1456
Crystal size	0.48 x 0.11 x 0.10 mm^3
Theta range for data collection	1.76 to 27.88°
Index ranges	$-14 \le h \le 14$
	$-29 \le k \le 29$
	$-17 \le l \le 17$
Reflections collected	32805
Independent reflections	8175 [R(int) = 0.0650]
Completeness to theta = 27.88°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9801 and 0.9095
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8175 / 0 / 453
Goodness-of-fit on F^2	0.948
Final R indices [I>2sigma(I)]	R1 = 0.0562, wR2 = 0.0759
R indices (all data)	R1 = 0.1661, wR2 = 0.0949
Largest diff. peak and hole	0.274 and -0.317 e.Å^{-3}

2.3. Calculation details

The conformation analysis and structural stability of the optimized geometry of the title compound studies was performed by Spartan 06 program package on a double Xeon/3.2 GHz processor with 8 GB RAM [30]. The molecular structure of the title compound, in the ground state, are optimized by using HF, BLYP, and B3LYP methods with the standard 6-31G* basis set.

3. Results and Discussion

The synthesis involves the reaction of a biphenyl-4-carbonyl chloride with potassium thiocyanate in acetone followed by condensation of the resulting biphenyl-4-carbonyl isothiocyanate with a 6-methylpyridin-2-amine (Scheme 1). The compound were purified by re-crystallization from an ethanol:dichloromethane mixture (1:2) and characterized by elemental analysis, NMR and FT-IR methods. The analytical data is consistent with the proposed structure given in Scheme 1.

The molecular structure and unit cell diagram of the title compound is shown in Figure 1 and 2, respectively, and selected bond lengths and angles are given in Table 2 and 3, respectively.

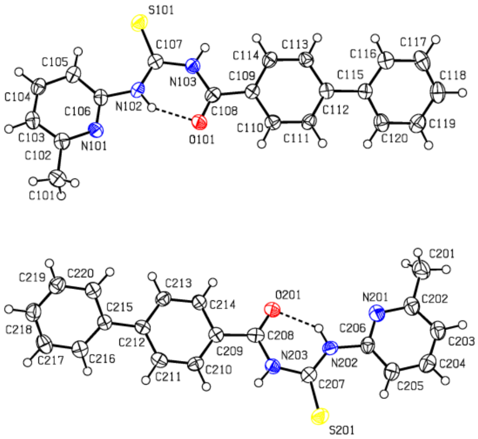
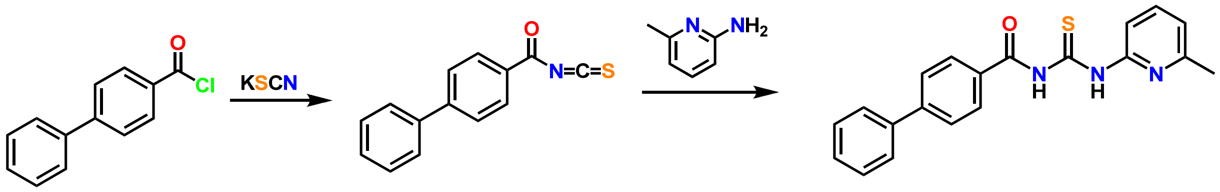


Figure 1. The molecular structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

The bond lengths are in normal ranges for the title compound [31,32]. The asymmetric unit of the title compound contains two crystallographically independent molecules A (atom numbering 1xx) and B (2xx). There is very little difference between the bond lengths and angles of these molecules. The bond lengths and angles in the thiourea moiety are typical for thiourea derivatives; the C107-S101, C207-S201, C108-O101 and C208-O201 bonds both show a typical double-bond character with 1.654(3), 1.652(3), 1.221(3) and 1.214(3) Å, respectively. The short bond lengths of the N102-C107, 1.335(3); N103-C107, 1.396(3), N103-C108, 1.382(3), N202-C207, 1.333(3); N203-C207, 1.395(3), and N203-C208, 1.387(3) Å bonds indicate that partial double bond character in this fragment. These results can be explained by the existence of resonance in this part of the molecule. The other C-N bond length is of expected range.

The torsion angles of C108-N103-C107-N102 and C208-N203-C207-N202 are -0.1(4) and 8.1(4)^o, respectively. The difference in the torsion angles can be attributed to the different conformations of the two independent molecules. Also, each of the molecular conformations are stabilized by an intramolecular N-H•••O hydrogen bonding interaction (Table 4), forming a planar six-membered ring (Figure 1). The maximum deviation for O201-C208-N203-C207-N202-H20D and O101-C108-N103-C107-N102-H10D six-membered rings are 0.080(3) Å for atom N203, and 0.010(3) Å for atom S101, respectively. These results also confirm the different conformations of the two independent molecules. A significant number of substitute benzoylthiourea derivatives have syn-anti configurations [32-38]. This configuration in each conformation of the title compound was observed.



Scheme 1

Table 2. Optimized and experimental bond lengths (Å) of the title compound in the ground state.

Parameters*	Experimental		Calculated		
			HF	DFT	
	Molecule A	Molecule B		BLYP	B3LYP
S1-C20	1.654(3)	1.652(3)	1.676	1.691	1.677
O2-C21	1.221(3)	1.214(3)	1.200	1.246	1.231
N3-C12	1.338(3)	1.335(3)	1.322	1.352	1.339
N3-C19	1.326(3)	1.336(3)	1.318	1.354	1.340
N4-C19	1.416(3)	1.413(3)	1.412	1.419	1.410
N4-C20	1.335(3)	1.333(3)	1.327	1.363	1.349
N6-C20	1.396(3)	1.395(3)	1.387	1.420	1.406
N6-C21	1.382(3)	1.389(4)	1.379	1.400	1.387
C8-C12	1.485(4)	1.499(4)	1.507	1.520	1.509
C12-C13	1.390(4)	1.384(4)	1.387	1.411	1.400
C13-C15	1.373(4)	1.369(4)	1.383	1.404	1.393
C15-C17	1.382(4)	1.387(3)	1.382	1.401	1.393
C17-C19	1.389(4)	1.381(4)	1.388	1.412	1.400
C21-C22	1.486(4)	1.490(4)	1.493	1.501	1.494
C22-C23	1.384(4)	1.386(3)	1.390	1.413	1.402
C22-C30	1.390(3)	1.384(4)	1.391	1.414	1.402
C23-C25	1.381(4)	1.378(4)	1.381	1.398	1.389
C25-C27	1.393(4)	1.394(4)	1.394	1.418	1.406
C27-C28	1.395(4)	1.386(4)	1.392	1.417	1.406
C27-C32	1.482(4)	1.477(4)	1.490	1.491	1.484
C28-C30	1.376(4)	1.382(4)	1.382	1.400	1.391
C32-C33	1.387(4)	1.389(4)	1.391	1.416	1.405
C32-C41	1.390(4)	1.383(4)	1.392	1.417	1.405
C33-C35	1.383(4)	1.394(4)	1.385	1.404	1.394
C35-C37	1.381(4)	1.373(4)	1.395	1.406	1.395
C37-C39	1.375(4)	1.375(4)	1.395	1.406	1.396
C39-C41	1.378(4)	1.382(4)	1.385	1.403	1.394
r (Exp Molecule A-Theor)			0.9957	0.9950	0.9960
r (Exp Molecule B-Theor)			0.9938	0.9928	0.9940

* The structure parameters are in accordance with the atom numbering scheme given in Figure 3.

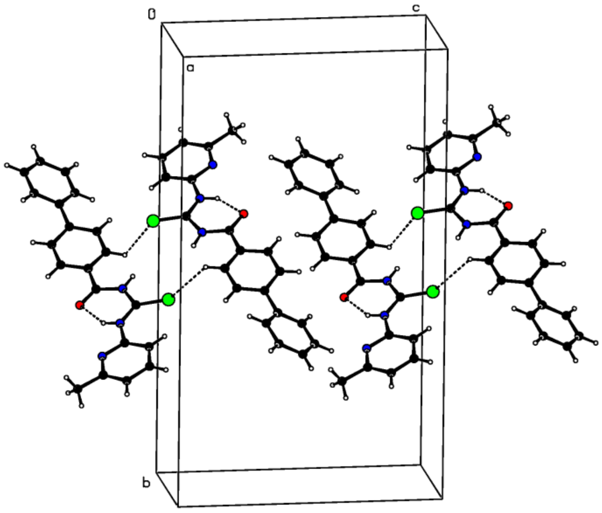


Figure 2. Unitcell diagram of *N*-(6-methylpyridin-2-ylcarbamothioyl) biphenyl-4-carboxamide.

We performed full geometry optimization of the title compound. The optimized structure parameters of the title compound calculated by ab initio and DFT methods listed in Table 2 and 3 and are in accordance with atom numbering scheme given in Figure 3. Table 2 and 3 compare the calculated geometric parameters with the experimental data.

Based on this comparison, the bond lengths and angles calculated for the title compound show good agreement with the experimental results. However, based on our calculations, the optimized bond lengths and angles obtained by DFT/B3LYP method show the best agreement with the experimental values. The largest difference between experimental and calculated DFT/B3LYP-6-31G* bond length and angle is 0.024 Å and 1.42°, respectively.

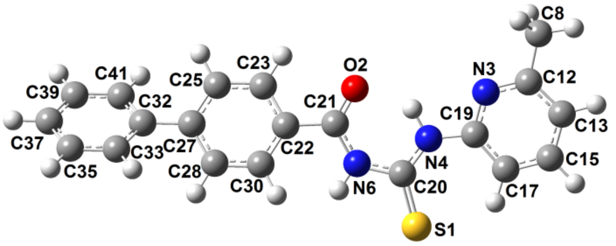


Figure 3. The lowest energy optimized conformer of the title compound calculated at B3LYP/6-31G* level.

Table 3. Optimized and experimental bond angles (°) of the title compound in the ground state.

Parameters*	Experimental		Calculated		
			HF	DFT	
	Molecule A	Molecule B		BLYP	B3LYP
C12-N3-C19	117.7(3)	117.7(3)	119.92	118.72	119.12
C19-N4-C20	132.7(3)	132.0(3)	132.92	132.56	132.53
C20-N6-C21	129.4(3)	129.3(3)	130.65	130.42	130.32
N3-C12-C8	116.3(3)	116.3(3)	116.23	116.07	116.20
N3-C12-C13	122.4(3)	122.4(3)	121.61	121.90	121.74
C8-C12-C13	121.3(3)	121.3(3)	122.16	122.03	122.06
C12-C13-C15	118.5(3)	118.7(3)	118.03	118.62	118.57
C13-C15-C17	120.3(3)	120.5(3)	120.62	120.21	120.22
C15-C17-C19	116.6(3)	116.3(3)	116.55	116.95	116.88
N3-C19-N4	110.8(3)	110.4(3)	110.36	110.73	110.80
N3-C19-C17	124.5(3)	124.5(3)	123.27	123.59	123.46
N4-C19-C17	124.7(3)	125.1(3)	126.37	125.68	125.73
S1-C20-N4	128.6(2)	128.4(2)	128.93	129.63	129.44
S1-C20-N6	117.7(2)	117.3(2)	115.86	117.61	117.49
N4-C20-N6	113.7(2)	114.3(2)	115.21	114.76	113.07
O2-C21-N6	122.3(3)	121.8(3)	122.91	122.46	122.65
O2-C21-C22	122.0(3)	122.2(3)	121.69	121.77	121.75
N6-C21-C22	115.7(3)	115.9(3)	115.39	115.76	115.60
C21-C22-C23	117.1(3)	116.7(3)	117.30	117.35	117.26
C21-C22-C30	124.8(3)	124.9(3)	123.70	124.17	123.98
C23-C22-C30	118.1(3)	118.4(3)	118.98	118.46	118.75
C22-C23-C25	121.1(3)	120.4(3)	120.49	120.78	120.59
C23-C25-C27	121.3(3)	121.8(3)	120.89	121.23	121.10
C25-C27-C28	116.8(3)	116.9(3)	118.27	118.66	116.90
C25-C27-C32	122.0(3)	122.0(3)	120.86	121.30	121.08
C28-C27-C32	121.2(3)	121.0(3)	120.87	121.04	121.02
C27-C28-C30	122.0(3)	121.6(3)	121.00	121.25	121.17
C22-C30-C28	120.4(3)	120.6(3)	120.36	120.63	120.49
C27-C32-C33	120.5(3)	120.2(3)	120.74	120.96	120.91
C27-C32-C41	121.2(3)	120.9(3)	120.64	121.00	120.91
C33-C32-C41	118.2(3)	118.9(3)	118.62	118.05	118.19
C32-C33-C35	120.8(3)	120.4(3)	120.72	120.99	120.94
C33-C35-C37	119.9(3)	119.7(3)	120.18	120.27	120.21
C35-C37-C39	120.0(3)	120.2(3)	119.62	119.40	119.53
C37-C39-C41	119.9(3)	120.2(3)	120.21	120.36	120.26
C32-C41-C39	121.1(3)	120.5(3)	120.66	120.93	120.88
r (Exp Molecule A-Theor)			0.9783	0.9895	0.9911
r (Exp Molecule B-Theor)			0.9801	0.9881	0.9883

* The structure parameters are in accordance with the atom numbering scheme given in Figure 3.

The main difference between the two independent molecules of the title compound is torsion angles of CX08-NX03-CX07-NX02. Thus, the optimized molecule was submitted to a conformation analysis. For calculation of the potential energy as a function of the CX08-NX03-CX07-NX02 torsion angle, the θ was varied from 0 o to 360 ° with a grid size of 10°. The results are given in Figure 4. A total of three minima were located from the potential energy curve. The global minimum observed at θ = 0° (Oxygen and sulfur atoms are in anti position) with -884832.34 kcal/mol, while the other two minima, 19.22 kcal/mol and 18.64 kcal/mol higher in energy at θ = 140° and θ = 220°, respectively, corresponding to the global minimum. Although the structures of these two minimas do not agree with the conformations found in the crystal structure, these two minimum energy states can be explain by the electrostatic repulsion.

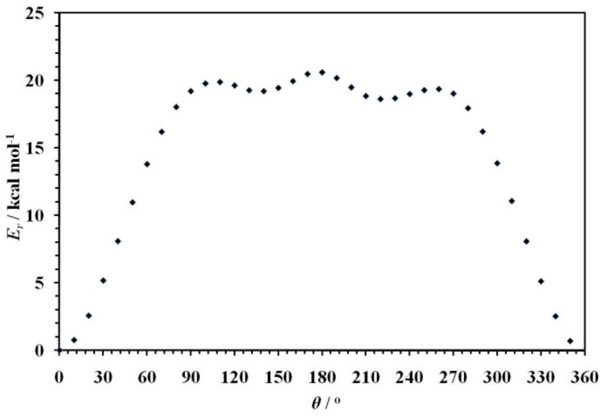


Figure 4. The potential energy curve of optimized structure of the title compound by rotating *θ* (N4/C20/N6/C21) from 0° to 360° (DFT/B3LYP/6-31G*).

The obtained results on the torsion angle at 0° agree with the single crystal structure data and an intramolecular N-H•••O hydrogen bonding interaction. In addition, the points on the energy curve at θ = 110° (ΔE = 19.90 kcal/mol), 180° (ΔE = 20.62 kcal/mol) (Oxygen and sulfur are in syn position) and 260° (ΔE = 19.37 kcal/mol) torsion angles cannot form an intramolecular N-H•••O hydrogen bonding interaction, thus they exist at higher energy states. The calculated energy value at θ = 8.1° with DFT/B3LYP/6-31G* is -1410.0905584 au (ΔE = 0.52 kcal/mol). Since the energy barrier between the observed two conformers (θ = -0.1 and 8.1°) from single crystal X-ray diffraction study is lower than 0.6 kcal/mol (RT), some inter-conversion can be expected. This energy values explain two crystallographically independent molecules A and B in the crystal structure of the title compound.

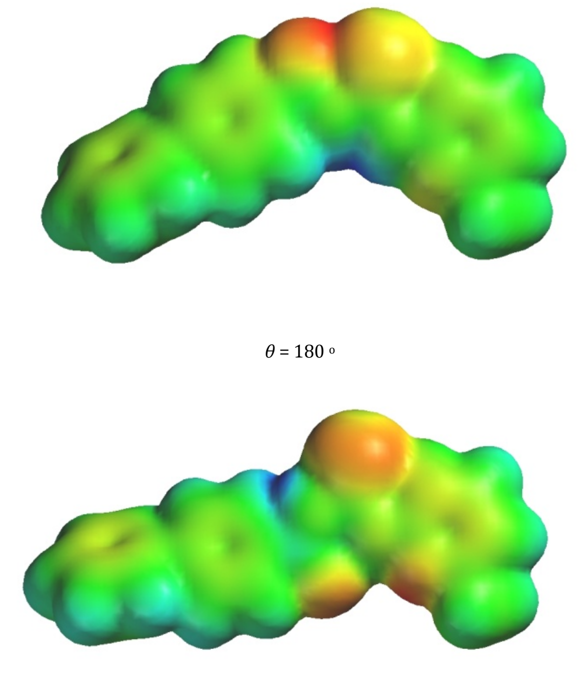
Table 4. Hydrogen-bond geometry (Å, °).

D*—H⋯*A	***D*—H**	**H⋯*A***	***D*⋯*A***	***D*—H⋯*A***
N102—H10D⋯O101	0.88	1.86	2.625(3)	144
N202—H20D⋯O201	0.88	1.89	2.637(3)	142
N103 H10E S201^{i}	0.88	2.95	3.718(2)	146.9
N203 H20E S101^{ii}	0.88	2.99	3.817(2)	158.2

Symmetry codes, i: x, y, 1+z; ii: x, y, -1+z.

The molecular electrostatic potential maps were calculated using the Spartan 06 program package graphic module for θ = 0° (*anti*) and 180° (*syn*) conformers with the minimum and the maximum energy states, respectively. The molecular electrostatic potential surfaces of the conformers of the title compound are electrostatic potentials encoded onto total electron density surface of constant electron density (0.002 e/a.u.^{3}). The molecular electrostatic potential maps of the conformers are presented in Figure 5.

These molecular electrostatic potential maps provide the isosurface values with the location of negative and positive electrostatic potentials. The differences between nucleo philicity and electrophilicity may affect its the proton donating or accepting ability of the compound. This, in turn, may influence the intermolecular hydrogen bond formation. As seen in Figure 5, the negative and positive potentials in the *anti* structure are dispersing more homogeneously than the *syn*-structure. In addition, the calculated dipole moment values (*syn*-conformer = 6.316 Debye and *anti*-conformer = 3.203 Debye) are in agreement with these results. The single crystal X-ray diffraction study confirms the existence of weak intermolecular hydrogen bonds in the title compound. Thus, the molecular electrostatic potential maps are confirmed the global minimum (*anti*) and maximum (*syn*) energy state.



θ = 180 °

θ = 0 °

Figure 5. Molecular electrostatic potential maps encoded onto total electron density surface of the two conformer of the title compound (deepest red and deepest blue are show the most negative and the most positive potential regions, respectively).

Acknowledgement

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Supplementary material

CCDC-761452 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or 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(0)1223-336033.

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