

Crystal Structure of 3-Benzyl-4-(3-methyl-3-phenylcyclobut-1-yl)-1,3-thiazole-2(3H)-thione

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Received: 25 June 2015;	Accepted: 3 August 2015;	Published online: 5 December 2015;	AJC-17665
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The title compound 3-benzyl-4-(3-methyl-3-phenylcyclobut-1-yl)-1,3-thiazole-2(3*H*)-thione having m.f. $C_{21}H_{21}NS_2$, crystallizes in the orthorhombic space group Pna2₁, Z = 4 with a = 10.1027(5) Å, b = 17.3913(8) Å, c = 10.8832(6) Å, V = 1912.17(17) Å³ and D_{calc} = 1.221 g/cm³. In the title molecule, the cyclobutane ring is puckered, with a dihedral angle of 23.78(18)° between the two planes. The thiazole ring makes dihedral angles of 84.23(11), 55.58(16) and 88.08(10)°, respectively, with the benzene, cyclobutane and phenyl rings. Weak intramolecular C–H…S and C–H…N hydrogen-bonding interactions are present in the molecule. Each of these interactions forms a five-membered ring. The supramolecular aggregation is completed by two types of C–H… π interactions involving the H atoms from C5 and C20 atoms.

Keywords: Crystal structure, Cyclobutane, 1,3-Thiazole-2(3H)-thione.

INTRODUCTION

It is well known that 3-substituted cyclobutane carboxylic acid derivatives exhibit anti-inflamatory and antidepressant activities and liquid crystal properties [1]. Compounds, containing cyclobutane and thiazole, seem to be suitable candidates for further chemical modifications and pharmacologically active may have herbicidal, anti-inflamatory, anti-microbial, or antiparasitic activity. Besides, useful as ligands in coordination chemistry [2] so that various 1,3-thiazolidine-2-thione both nitrogen and sulphur coordination to metals has been confirmed [3].

EXPERIMENTAL

The synthesis, crystallization and spectroscopic studies of 3-benzyl-4-(3-methyl-3-phenylcyclobut-1-yl)-1,3-thiazole-2(3*H*)-thione has been reported previously [4]. A suitable single crystal of title compound for data collection was selected and data were collected at 293(2) K by ω -scan technique, on an Agilent Diffraction Xcalibur X-ray diffractometer with an Eos CCD area detector using graphite-monochromated radiation MoK_{α} (λ =0.71073 Å) from a enhance X-ray source. The data collection, cell refinement and data reduction were performed using the CrysAlis^{Pro} program [5]. Solution, refinement and analysis of the structure were done using the OLEX2 system [6]. The crystal structure was solved by the direct method using the SHELXS-97 [7] and refined by full-matrix least squares method based on F^2 against all reflections using the SHELXL-97 [7]. The refinement converged to $R_1 = 0.0378$; w $R_2 = 0.0707$ and S = 1.034 for 2255 reflections with I > 26(I) and $R_1 = 0.0514$; w $R_2 = 0.0760$ and S = 1.034 for 2757 unique reflections and 218 parameters. All non-hydrogen atoms were refined anisotropically. The crystal structure positions of hydrogen atoms were treated as riding atoms. Geometrical calculations were performed using PLATON [8]. The figures were made using ORTEP [9] and PLATON [8]. The summary of the crystal data, experimental details and refinement results are listed in Table-1.

RESULTS AND DISCUSSION

In the structure of title compound (Fig. 1), the phenyl and thiazole rings are *cis*-related with respect to the cyclobutane ring. The steric interaction between the substituent groups on the cyclobutane ring means that this ring deviates significantly from planarity. Values for the puckering of the cyclobutane have been reported as 23.5-24.3° [10,11]. The cyclobutane ring is distinctly puckered, with a dihedral angle between C7/C8/C10 plane and C8/C9/C10 plane of 23.78(18)°. The bond distances and angles in the cyclobutane ring are similarity in good agreement with the literature values (Table-2) [12-14].

The thiazole \longrightarrow thione system is reasonably planar, the maximum deviation from planarity being 0.0067(19) Å for atom N1. The C13–S1–C14 bond angle of 91.70(16)°

	TABLE-1
	CRYSTAL DATA AND STRUCTURE REFINEMENT
	PARAMETERS FOR THE TITLE COMPOUND
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Chemical formula	$C_{21}H_{21}NS_2$		
Formula weight	351.51		
Temperature (K)	293(2)		
Space group	Pna2 ₁		
Crystal system	Orthorhombic		
a, b, c (Å)	10.1027(5), 17.3913(8),		
	10.8832(6)		
α, β, γ (°)	90, 90, 90		
Cell volume (Å ³)	1912.17(17)		
Formula unit cell Z	4		
$\rho_{calc}(g/cm^3)$	1.221		
F(000)	744.0		
Absorption coefficient μ (mm ⁻¹)	0.280		
Crystal size (mm ³)	$0.4648 \times 0.4513 \times 0.2234$		
Diffractometer	Xcalibur, Eos		
Radiation/Wavelength (Å)	$MoK_{\alpha} / (\lambda = 0.71073)$		
Reflections measured	6170		
Range of h, k, l	$-12 \le h \le 10, -16 \le k \le 21,$		
	-8≤1≤13		
Data/Restraints/Parameters	2757/1/218		
Final R indexes $[I \ge 2\sigma(I)]$	R1 = 0.0378, wR2 = 0.0707		
Final R indexes [all data]	R1 = 0.0514, $wR2 = 0.0760$		
Goodness-of-fit on F ²	1.034		
Largest diff. peak/hole (e Å-3)	0.22/-0.17		
Flack parameter	-0.02(6)		



Fig. 1. Molecular structure and atom-numbering scheme for the title compound. Displacement ellipsoids are shown at the 50 % probability level

TABLE-2 SELECTED GEOMETRIC PARAMETERS (Å °)					
S2 C14 1668(3) C14 N1 C12 115 0(2)					
N1-C12	1.411(4)	C12-C13-S1	112.4(3)		
N1-C14	1.357(4)	N1-C14-S1	109.4(2)		
C7–C8	1.550(4)	C7–C8–C9	89.7(2)		
C7-C10	1.560(5)	C10C9C8	88.0(2)		
C8–C9	1.555(4)	C8-C7-C10	87.8(2)		
C9-C10	1.550(4)	C9-C10-C7	89.5(2)		

shows that the heterocyclic ring is distorted from a regular pentagon. The S1–C13 and S1–C14 bond lengths are 1.723 (3) Å and 1.727 (3) Å. These values are shorter than the standard value for an S–C sp^2 single bond (1.76 Å) [15] and comparable with those related structures [16-18]. The C2–S2 bond length is close to the corresponding value reported in the literature [19-21].

The dihedral angles between the thiazole plane A (S1/N1/C12–C14), the benzene plane B (C16–C21), the cyclobutane

plane C (C7–C10) and the phenyl plane D (C1–C6) are $84.23(11)^{\circ}$ (A/B), $55.58(16)^{\circ}$ (A/C), $88.08(10)^{\circ}$ (A/D), $80.24(17)^{\circ}$ (B/C), $64.20(14)^{\circ}$ (B/D) and $40.19(14)^{\circ}$ (C/D).

There are no classical hydrogen bonds observed in the crystal structure. The molecular structure is stabilized by C15–H15A…S2 and C17–H17…N1 intramolecular interactions, both of which are generate S(5) ring motifs (Table-3) [22]. In addition, two weak intermolecular C–H… π interactions are also present, consolidating the molecules into a three-dimensional network (Fig. 2). Details of these interactions are given Table-4.

TABLE-3 HYDROGEN-BOND GEOMETRY (Å, °)					
D–H···A	D–H	H…A	D…A	D–H…A	
C15-H15A…S2	0.97	2.69	3.131(3)	108	
C17-H17…N1	0.93	2.60	2.908(4)	100	



Fig. 2. Crystal packing viewed along the c axis showing weak intermolecular C-H \cdots π interactions as dashed lines

TABLE-4					
GEOMETRIC PARAMETERS (Å, °) FOR C-H…π					
CONTACTS IN THE TITLE STRUCTURE					
C–H…Cg	H–Cg ^a	H _{perp} ^b	γ ^c	C–H…Cg	C…Cg
C5–H5····Cg ⁱ	2.78	-2.76	6.90	156	3.648(4)
C20-H20···Cg ⁱⁱ	2.79	2.77	6.79	158	3.673(4)

Notes: (a) Cg1–Cg2 are, respectively, the centroids of the benzene rings defined by atoms C16–C21 and C1–C6; (b) H_{perp} is the perpendicular distance of H from the π –acceptor ring; (c) γ is the angle at H between H···Cg and H_{perp}. Symmetry codes: (i) 1-x,1-y,-1/2+z; (ii) 3/2-x,-1/2+y,1/2+z

Supplementary material

CCDC 1401448 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/cif.

ACKNOWLEDGEMENTS

The authors acknowledge to Dokuz Eylul University for the use of the Agilent Xcalibur Eos difractometer (purchased under University Research Grant No: 2010.KB.FEN.13).

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