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#### Abstract

The title compound 3-benzyl-4-(3-methyl-3-phenylcyclobut-1-yl)-1,3-thiazole-2 $\left(3 H\right.$ )-thione having m.f. $\mathrm{C}_{21} \mathrm{H}_{21} \mathrm{NS}_{2}$, crystallizes in the orthorhombic space group Pna $2_{1}, \mathrm{Z}=4$ with $\mathrm{a}=10.1027(5) \AA, \mathrm{b}=17.3913(8) \AA, \mathrm{c}=10.8832(6) \AA, \mathrm{V}=1912.17(17) \AA^{3}$ and $\mathrm{D}_{\text {calc }}=1.221$ $\mathrm{g} / \mathrm{cm}^{3}$. In the title molecule, the cyclobutane ring is puckered, with a dihedral angle of $23.78(18)^{\circ}$ between the two planes. The thiazole ring makes dihedral angles of $84.23(11), 55.58(16)$ and $88.08(10)^{\circ}$, respectively, with the benzene, cyclobutane and phenyl rings. Weak intramolecular $\mathrm{C}-\mathrm{H} \cdots \mathrm{S}$ and $\mathrm{C}-\mathrm{H} \cdots \mathrm{N}$ hydrogen-bonding interactions are present in the molecule. Each of these interactions forms a fivemembered ring. The supramolecular aggregation is completed by two types of $\mathrm{C}-\mathrm{H} \cdots \pi$ interactions involving the H atoms from C 5 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$2(3 \mathrm{H})$-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 $\omega$-scan technique, on an Agilent Diffraction Xcalibur X-ray diffractometer with an Eos CCD area detector using graphite-monochromated radiation $\operatorname{MoK}_{\alpha}(\lambda=0.71073 \AA)$ from a enhance X-ray source. The data collection, cell refinement and data reduction were performed using the CrysAlis ${ }^{\text {Pro }}$ 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 $\mathrm{F}^{2}$ against all reflections using the SHELXL-97 [7]. The refinement converged to $\mathrm{R}_{1}=0.0378$; $\mathrm{wR}_{2}=0.0707$ and $\mathrm{S}=1.034$ for 2255 reflections with $\mathrm{I}>20$ (I) and $R_{1}=0.0514 ; \mathrm{wR}_{2}=0.0760$ and $\mathrm{S}=1.034$ 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 $23.5-24.3^{\circ}$ [10,11]. The cyclobutane ring is distinctly puckered, with a dihedral angle between $\mathrm{C} 7 /$ C8/C10 plane and C8/C9/C10 plane of $23.78(18)^{\circ}$. The bond distances and angles in the cyclobutane ring are similarity in good agreement with the literature values (Table-2) [12-14].

The thiazole $\rightleftharpoons$ thione system is reasonably planar, the maximum deviation from planarity being $0.0067(19) \AA$ for atom N1. The C13-S1-C14 bond angle of $91.70(16)^{\circ}$

| TABLE-1 |  |
| :---: | :---: |
| CRYSTAL DATA AND STRUCTURE REFINEMENT |  |
| PARAMETERS FOR | E TITLE COMPOUND |
| Chemical formula | $\mathrm{C}_{21} \mathrm{H}_{21} \mathrm{NS}_{2}$ |
| Formula weight | 351.51 |
| Temperature (K) | 293(2) |
| Space group | Pna $1_{1}$ |
| Crystal system | Orthorhombic |
| a, b, c ( $\AA$ ) | $\begin{aligned} & 10.1027(5), 17.3913(8), \\ & 10.8832(6) \end{aligned}$ |
| $\alpha, \beta, \gamma\left({ }^{\circ}\right)$ | 90, 90, 90 |
| Cell volume ( $\AA^{3}$ ) | 1912.17(17) |
| Formula unit cell Z | 4 |
| $\rho_{\text {calc }}\left(\mathrm{g} / \mathrm{cm}^{3}\right)$ | 1.221 |
| $\mathrm{F}(000)$ | 744.0 |
| Absorption coefficient $\mu\left(\mathrm{mm}^{-1}\right)$ | 0.280 |
| Crystal size ( $\mathrm{mm}^{3}$ ) | $0.4648 \times 0.4513 \times 0.2234$ |
| Diffractometer | Xcalibur, Eos |
| Radiation/Wavelength (Å) | $\mathrm{MoK}_{\alpha} /(\lambda=0.71073)$ |
| Reflections measured | 6170 |
| Range of h, k, l | $\begin{aligned} & -12 \leq h \leq 10,-16 \leq k \leq 21, \\ & -8 \leq 1 \leq 13 \end{aligned}$ |
| Data/Restraints/Parameters | 2757/1/218 |
| Final R indexes [ $\mathrm{I}>=2 \sigma(\mathrm{I})$ ] | $\mathrm{R} 1=0.0378$, $\mathrm{wR} 2=0.0707$ |
| Final R indexes [all data] | $\mathrm{R} 1=0.0514, \mathrm{wR} 2=0.0760$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.034 |
| Largest diff. peak/hole (e $\AA^{-3}$ ) | 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 $\left(\AA,{ }^{\circ}\right)$ |  |  |  |
| S2-C14 | $1.668(3)$ | 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 | $1.560(5)$ | C10-C9-C8 | $88.0(2)$ |
| C8-C9 $9-C 10$ | $1.555(4)$ | 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) $\AA$ and 1.727 (3) $\AA$. These values are shorter than the standard value for an S-C $s p^{2}$ single bond ( $1.76 \AA$ ) [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/ $\mathrm{N} 1 / \mathrm{C} 12-\mathrm{C} 14)$, the benzene plane $\mathrm{B}(\mathrm{C} 16-\mathrm{C} 21)$, the cyclobutane
plane $\mathrm{C}(\mathrm{C} 7-\mathrm{C} 10)$ and the phenyl plane $\mathrm{D}(\mathrm{C} 1-\mathrm{C} 6)$ are $84.23(11)^{\circ}(\mathrm{A} / \mathrm{B}), 55.58(16)^{\circ}(\mathrm{A} / \mathrm{C}), 88.08(10)^{\circ}(\mathrm{A} / \mathrm{D})$, $80.24(17)^{\circ}(\mathrm{B} / \mathrm{C}), 64.20(14)^{\circ}(\mathrm{B} / \mathrm{D})$ and $40.19(14)^{\circ}(\mathrm{C} / \mathrm{D})$.

There are no classical hydrogen bonds observed in the crystal structure. The molecular structure is stabilized by C15H15A $\cdots$ S2 and $\mathrm{C} 17-\mathrm{H} 17 \cdots \mathrm{~N} 1$ intramolecular interactions, both of which are generate $S(5)$ ring motifs (Table-3) [22]. In addition, two weak intermolecular $\mathrm{C}-\mathrm{H} \cdots \pi$ 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 $\left(\AA,{ }^{\circ}\right)$ |  |  |  |  |  |
| $\mathrm{D}-\mathrm{H} \cdots \mathrm{A}$ | $\mathrm{D}-\mathrm{H}$ | $\mathrm{H} \cdots \mathrm{A}$ | $\mathrm{D} \cdots \mathrm{A}$ | $\mathrm{D}-\mathrm{H} \cdots \mathrm{A}$ |  |
| $\mathrm{C} 15-\mathrm{H} 15 \mathrm{~A} \cdots \mathrm{~S} 2$ | 0.97 | 2.69 | $3.131(3)$ | 108 |  |
| $\mathrm{C} 17-\mathrm{H} 17 \cdots \mathrm{~N} 1$ | 0.93 | 2.60 | $2.908(4)$ | 100 |  |



Fig. 2. Crystal packing viewed along the c axis showing weak intermolecular $\mathrm{C}-\mathrm{H} \cdots \pi$ interactions as dashed lines

| TABLE-4 <br> GEOMETRIC PARAMETERS $\left(\AA \AA,{ }^{\circ}\right)$ FOR C-H $\cdots \pi$ <br> CONTACTS IN THE TITLE STRUCTURE |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C}-\mathrm{H} \cdots \mathrm{Cg}$ | ${\mathrm{H}-\mathrm{Cg}^{\mathrm{a}}}^{\mathrm{C}}$ | $\mathrm{H}_{\text {perp }}{ }^{\mathrm{b}}$ | $\gamma$ | $\mathrm{C}-\mathrm{H} \cdots \mathrm{Cg}$ | $\mathrm{C} \cdots \mathrm{Cg}$ |
| $\mathrm{C} 5-\mathrm{H} 5 \cdots \mathrm{Cg}$ | 2.78 | -2.76 | 6.90 | 156 | $3.648(4)$ |
| $\mathrm{C} 20-\mathrm{H} 20 \cdots \mathrm{Cg}^{\mathrm{ii}}$ | 2.79 | 2.77 | 6.79 | 158 | $3.673(4)$ |

Notes: (a) $\mathrm{Cg} 1-\mathrm{Cg} 2$ are, respectively, the centroids of the benzene rings defined by atoms $\mathrm{C} 16-\mathrm{C} 21$ and $\mathrm{C} 1-\mathrm{C} 6$; (b) $\mathrm{H}_{\text {perp }}$ is the perpendicular distance of H from the $\pi$-acceptor ring; (c) $\gamma$ is the angle at H between $\mathrm{H} \cdots \mathrm{Cg}$ and $\mathrm{H}_{\text {perp }}$. Symmetry codes: (i) $1-\mathrm{x}, 1-\mathrm{y},-1 / 2+\mathrm{z}$; (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.

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