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Crystal and molecular structure of *o*-thiobenzyl-N,N-dibenzylaniline ($C_{27}H_{25}NS$)

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In crystals of *o*-thiobenzyl N,N-dibenzylaniline (I) ($C_{27}H_{25}NS$), there are three benzyl groups. N atom is two covalent with the C atoms of the two benzyl groups and the S atom is covalent with the C atom of the other benzyl group. The distances N1-C21, N1-C14 and S1-C7 have been found to be 1.489(4), 1.488(9) and 1.832(8)Å, respectively. The molecule is as a whole non-planar. The S1 and the N1 atoms make intramolecular hydrogen bonding. No intermolecular hydrogen bonding has been found and the molecules are stabilised by the network of Van der Waals interaction in their crystalline assembly.

[**Keywords:** $C_{27}H_{25}NS$, Van der Walls interactions, Crystal structure of $C_{27}H_{25}NS$, Molecular structure of $C_{27}H_{25}NS$]
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1 Introduction

The compound *o*-thiobenzyl-N,N-dibenzylaniline ($C_{27}H_{25}HS$) (I) is used as a precursor for the synthesis of azobenzene-2-sulphenyl compounds, a class of biligated organic sulphur compounds having interesting properties. Baeyer's condensation of appropriate nitroso compounds with *o*-thiobenzyl-N,N-dibenzyl-aniline give fair yield of respective azobenzene derivatives which on brominolysis yield azobenzene-2-sulphenyl bromides. The proximity of the sulphur atom to the ortho-azo group leads to sulphur-azo interaction[1] thereby imparting stability to the compound. The ortho-azo interaction was also seen in the compound 2′-chloroazobenzene-2-sulphenylbromide[2]. The title compound has been undertaken in order to study the effect of the bulky ortho N,N-dibenzyl group on the spatial orientation of the S-benzyl group at the adjacent carbon.The detailed crystal data of the title compound are presented in Table 1.

2 Experimental Details

A solution of 2-aminothiophenol (0.08 m, 80 ml of ethanol) was taken and to it an aqueous solution of sodium hydroxide (0.1 m, 100 ml of water) was added. The mixture was refluxed. To the above mixture, 11.5 ml of benzylchloride was added. Boiling was continued for 45 min and allowed to stand overnight. Both the nucleophilic sites -NH2 and -SH were benzylated to produce *o*-thiobenzyl N,N-dibenzyl aniline. Colourless crystals were obtained which were washed with water and re-crystallised from ethanol.

Table 1—Crystal data of *o*-thiobenzyl N,N-dibenzylaniline ($C_{27}H_{25}NS$)

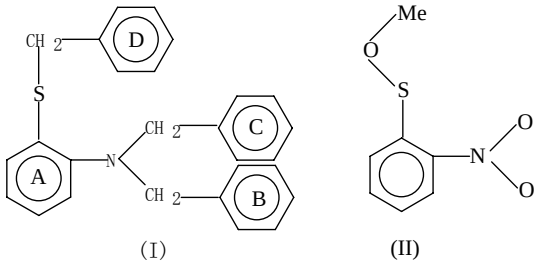
Chemical name	: *o*-thiobenzyl N,N-dibenzylaniline
Chemical formula	: $C_{27}H_{25}NS$
Molecular weight	: 395.54
Crystal system	: monoclinic
Space group	: $P2_1/a$
Lattice parameters	: a = 9.485(11) Å
	: b = 16.43(7) Å
	: c = 14.32(4) Å
	: β=90.100(9)
Measured density, D_m	: 1.177 Mg m^{-3}
Calculated density	: 1.173 Mg m^{-3}
No. of molecules per unit cell	: 4
λ (CuK_α)	: 1.5418 Å
μ (CuK_α)	: 1.359 mm^{-1}
R_{int}	: 0.0490
Crystal size	: 0.56×0.31×0.12 mm^3
Crystal colour	: Colourless
Data collection	: CAD-4 automated diffractometer with ω-2θ (Ref 4)
Absorption correction	: Ψ-scan (Ref. 5)
Temperature	: 293 K
No. of reflections measured	: 3742
No. of unique reflections	: 2073
No. of observed reflections	: 1511
Observed criteria	: $I > 2\sigma(I)$

θ_{max} = 67, h = 0→11, k = 0→19, l = -16→16, 4 standard reflections after every 500 reflections were measured; intensity decay none.

3 Discussion

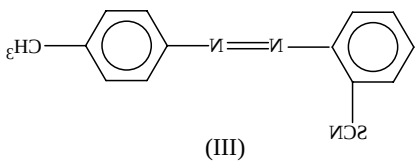
In *o*-thiobenzyl-N,N-dibenzylaniline (I) two resonance donating groups benzylthio and dibenzylamino groups are located at *ortho*-positions of benzene ring A (Fig. 1). In comparison with other related compounds viz. methyl-2-nitrophenyl sulphate[4] (II) and 4′-methylazobenzene-2-sulphenyl-cyanide[5] (III) where electron withdrawing groups are present in *ortho*-positions, the geometrical parameters of the benzene ring in the title compound do not change except the C5-C6 [1.383(8) Å] and C1-C2 [1.389(8) Å] bond lengths which undergo elongation in the range of 0.02-0.03 Å. The electron releasing effect of the benzylthio and dibenzylamino group delocalizes the electrons in the ring and decreases the bond order of C5-C6 and C1-C2 bond, causing the observed elongation. The S1-C2 [1.772(5) Å] bond length is found to be shorter than the lower quartile of three connected carbon and two connected sulphur C-S bond [1.809(4) Å]. On the other hand, the C_{aryl}–N bond length N1-C1[1.433(6) Å] is found to be longer than the lower quartile value of such bonds [1.340(3) Å].

The shorter S1-C2 bond length, points to the fact that sulphur atom uses hybridized orbital in forming the σ-framework. This is supported by the fact that the bond angle i.e. C2-S1-C7 is appreciably higher (102.6(3)°) than 90°. This further supports that sulphur atom uses orbital containing appreciable s-character to form the σ-bonds. The C1-N1 bond length [1.433(6) Å] is shorter than the other two C-N bonds of the title compound due to use of nearly Sp^2-hybrid orbital of C1. Again the observed C1-N1 bond length is longer than the normal value, which may be due to the resonance electron releasing effect of the sulphur atom at ortho position having an effect on the overall hybridized state of C1.



(I)

(II)



(III)

The bond angle S1-C2-C1 is appreciably shorter [116.5(4)°] than the other related compounds[4,6,7]. This decrease in bond angle at C2 may be attributed to the necessity of sulphur atom to act as H-bond donor to undergo nearly symmetric weak interaction with H3 and H21A at (x, y, z), giving a tetra coordinated configuration of sulphur which plays a decisive role in determining the supra-molecular structure of the compound. Fractional atomic coordinates for non hydrogen atoms and equivalent isotropic displacement parameters (Å^2) are given in Table 2. The nitrogen atom also acts as a H-bond donor to three ortho hydrogen atoms. It gets involved in a nearly symmetric weak H-bonding interactions with H6, H20 and H27 at (x, y, z) of three benzene rings giving rise to a hexa-coordinated distorted octahedral configuration of the nitrogen atom.

Table 2—Fractional atomic coordinates for non hydrogen atoms and equivalent isotropic displacement parameters (Å^2)

$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

	x	*y*	*z*	U_{eq}
S1	0.24631(3)	0.33846(8)	0.03949(7)	0.0658(6)
N1	0.40762(4)	0.19625(2)	–0.00634(9)	0.0497(4)
C1	0.28991(5)	0.20654(3)	–0.06826(2)	0.0534(7)
C2	0.20312(5)	0.27351(3)	–0.05513(2)	0.0547(8)
C3	0.08761(5)	0.28730(3)	–0.11442(3)	0.0671(9)
C4	0.05891(6)	0.23224(4)	–0.18680(3)	0.0720(2)
C5	0.14520(7)	0.16552(4)	–0.19841(3)	0.0730(2)
C6	0.26051(5)	0.15181(3)	–0.14132(2)	0.0682(9)
C7	0.11502(6)	0.41970(4)	0.02872(3)	0.0760(2)
C8	0.13671(5)	0.47652(3)	0.10953(3)	0.0639(8)
C9	0.22420(7)	0.54362(4)	0.10381(4)	0.0760(3)
C10	0.24091(7)	0.59501(4)	0.17932(5)	0.1100(3)
C11	0.17192(8)	0.58013(4)	0.25934(5)	0.1060(3)
C12	0.08891(8)	0.51442(4)	0.26761(4)	0.1040(3)
C13	0.06830(6)	0.46361(3)	0.19203(3)	0.0860(2)
C14	0.43261(5)	0.11083(3)	0.02414(2)	0.0550(7)
C15	0.30831(4)	0.08244(3)	0.08370(2)	0.0531(5)
C16	0.22602(6)	0.01731(3)	0.05561(3)	0.0780(2)
C17	0.11170(6)	–0.00632(3)	0.11305(4)	0.0890(2)
C18	0.08701(6)	0.03044(3)	0.19613(3)	0.0820(2)
C19	0.17012(6)	0.09402(3)	0.22283(3)	0.0820(2)
C20	0.28044(5)	0.11942(3)	0.16612(3)	0.0730(2)
C21	0.53741(5)	0.23392(3)	–0.04551(2)	0.0690(2)
C22	0.65560(4)	0.24191(3)	0.02462(2)	0.0550(8)
C23	0.78522(5)	0.20381(3)	0.00970(3)	0.0672(2)
C24	0.89481(5)	0.21180(3)	0.07302(4)	0.0823(2)
C25	0.87623(6)	0.25802(4)	0.15181(3)	0.0790(2)
C26	0.75080(7)	0.29491(4)	0.16744(3)	0.0870(3)
C27	0.63862(5)	0.28804(3)	0.10505(3)	0.0730(2)

The dihedral angles between the phenyl ring A and the phenyl rings B, C and D are 74.4(2)°, 22.9(3)° and 87.7(4)°, respectively; suggests that the molecule is as a whole non-planar. The non-planarity of the molecule is also confirmed by the study of the torsion angles through the central bonds C7-C8, C14-C15 and C21-C22. The S1 and N1 atoms are planar with the phenyl ring A. The C7, C14 and the C21 atoms are in the plane passing through the respective phenyl rings to which they are attached. The two benzyl groups associated with N1 atoms are not planar and the dihedral angle between them is 57.0(2)°.

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