

Synthesis, Crystal Structure and Spectroscopic Studies of 1-(p-Bromophenyl)-3,5 Diphenylformazan

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Abstract: In this study, novel 1-substituted-phenyl-3,5-diphenylformazans were synthesized with -Br group at *p*-positions. Their structures were elucidated by elemental analyses, UV-vis and IR spectroscopy and X-ray single crystal structure determination. Their UV-vis spectra indicated that their λ_{\max} showed a shift amount of which was dependent upon the position of the substituent on the ring. The title compound, 1-(*p*-bromophenyl)-3,5 diphenylformazan, crystallizes in the orthorhombic P bca space group, with $a=7.9526(9)\text{Å}$, $b=18.611(2)\text{Å}$, $c=23.099(2)\text{Å}$. The final cycle of refinement was converged to $R = 0.0703$. The big part of the molecule is coplanar. The molecular conformation is maintained by an intramolecular N-H \cdots N hydrogen bond.

Keywords: Formazan, X-ray, organic compound, crystal structure.

INTRODUCTION

Formazans are compounds containing the characteristic azohydrazone group (-N=N-C=N-NH-), which is a good carrier of π -bonding and chelating properties. They are widely used as dyes, as ligands in complex formation reactions, and as analytical reagents, where their deep colour makes them good indicators of redox reactions [1, 2]. Formazans form salts and complexes with several metal ions, and especially the transition metal ions. Their derivatives with electron donating and withdrawing group attached to 1,3,5- phenyl ring were synthesized and the effects of substituents on the absorption λ_{\max} values were examined. They are also biologically active and there is much interest in their biological applications [3]. Various 1 and 3-substituted formazans were synthesized and, the effect of substituents evaluated by using UV-vis and IR spectra [4, 5]. The biological activity of formazan makes the knowledge of its oxidation potentials and possible mechanisms very important. In the present study, a novel formazan complex with substituent on 1-phenyl ring has been synthesized and its structure was determined using the X-ray diffraction method and characterized with spectroscopic techniques. The structure of formazan complex molecule is given in Fig. (1).

MATERIALS AND METHODOLOGY

General Procedures and Materials

All starting reagents and solvents were purchased from Merck, Sigma-Aldrich Chemical Co. and used without further purification. IR spectrum was recorded on a MATTSON 1000 FT-IR spectrophotometer with range 4000–625 cm^{-1}

using KBr pellets. Absorption spectra were obtained with UNICAM UV2-100 UV-vis spectrophotometer using 1 cm quartz cells in $10^{-4}\text{ mol l}^{-1}$ methanol in the range of 192.2–600 nm. Elemental analyses for (C, H, N) were performed using a LECO CHNS 932 elemental analyzer.

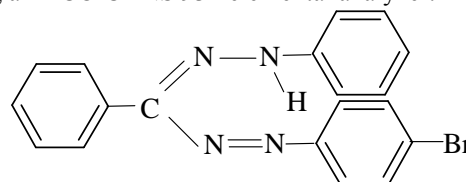


Fig. (1). Chemical diagram of 1-(*p*-bromophenyl)-3,5 diphenylformazan.

Synthesis of 1-(*p*-Bromophenyl)-3,5 Diphenylformazan

For the synthesis, dissolved Benzaldehyde (2.12 g, 0.02 mol) in 12.5 ml methanol was gradually added to phenylhydrazine (2.16g, 0.02 mol) with constant stirring at pH 5-6. The procedure was completed in 45 min. The resulting white hydrazone was left on the bench over night and was then filtered and recrystallized from methanol. The benzaldehyde phenylhydrazone (1.06 g, 0.01 mol) was dissolved in methanol (50ml). By constant stirring under reflux and buffer solution (prepared as before). In another flask, *p*-bromobenzenediazonium chloride solution was prepared using *p*-bromaniline (1.7203 g, 0.01 mol) concentrated HCl (2.5ml) and sodium nitrite (0.75g) at 0-5°C. This solution was added to the benzaldehyde phenylhydrazone solutions dropwise with constant stirring to form compound. The solution stirred to 2h at the same temperature and kept in a cupboard for 2 days. Dye was filtered and then washed water and methanol. The compound was recrystallised from dichloromethane. Red colored crystal; m.p 189 °C; yield 74%. Analysis calculated for $\text{C}_{19}\text{H}_{15}\text{BrN}_4$ (%): C, 60.16; H, 3.96; Br, 21.11; N, 14.76. Found (%): C, 60.12; H, 3.90; Br, 21.20; N, 14.79.

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RESULTS AND DISCUSSION

IR and UV-VIS Spectra of 1-(p-Bromophenyl)-3,5 Diphenylformazan

The most characteristics bands of the complex is summarized in Table 1. As seen from Table 1, $\nu(\text{C}=\text{N})$ bands at 1520-1500 cm^{-1} and $\nu(\text{N}=\text{N})$ bands at 1450-1410 cm^{-1} were observed in the complex. These results are in agreement with literature [4, 5]. The $\nu(\text{N}-\text{N})$ valans vibration bands observed in the region 1080, 1055 and 1030 cm^{-1} . Other aromatic $\nu(\text{C}-\text{H})$, $\nu(\text{C}=\text{C})$, $\nu(\text{CNNC})$ skeleton stretching bands in the compound were observed in their expecting regions. Table 2 list all peaks observed in the UV-vis spectra of 1-(p-bromophenyl)-3,5 diphenylformazan and the values of literature of 1, 3, 5 triphenylformazan at same solvent [6]. The chemical shift values ($\Delta \lambda_{\text{max}}$) were compared by taking the difference between the $\lambda_{\text{max}1}$ values of the *p*-Br substituted formazan with the λ_{max} value of TPF in this study. The peaks listed as $\lambda_{\text{max}1}$ in Table 2 are the broad peaks which are characteristic of the formazan skeleton. They are generally observed at 410–500 nm depending upon structure. These peaks are due to $\pi-\pi^*$ electronic transitions in the formazan skeleton. The sharp $\lambda_{\text{max}2}$ peaks which appear at 300–350 nm correspond to $n-\pi^*$ electronic transitions of the $-\text{N}=\text{N}-$ group. The $\lambda_{\text{max}3}$ peaks observed at 210–300 nm originate from $n-\pi^*$ transitions of $-\text{C}=\text{N}-$ groups. As seen from Table 2, the $\lambda_{\text{max}1}$ value of TPF at 483 nm, shifts to 489 nm when the 1-phenyl ring is substituted with a $-\text{Br}$ at the *p*-positions.

Description of the Crystal Structure of 1-(p-Bromophenyl)-3,5 Diphenylformazan

A needle red crystal with a size of 0.5x0.04x0,04 mm was used for diffraction experiments. Diffraction measurements were made at room temperature on a Stoe IPDS II CCD X-ray diffractometer using graphite-monochromated MoK_α radiation using ω -scan mode [7]. Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the $1.76 < \theta < 26$ range. The empirical absorption corrections were applied by the multiscan method *via* X-RED32 software. Data

collection, cell refinement and data reduction performed using STOE X-AREA and STOE X-RED [7,8]. The structure was solved by direct methods and refinement using the programs SHELXS97 and SHELXL97, respectively [9] in the WinGX package [10]. The quality of crystals obtained was always poor and this fact may underlie both low proportion of the reflection labelled “observed” at room temperature and fairly high merging index. A full-matrix least-squares refinement on F^2 converged at $R = 0.0703$. All non-hydrogen atoms were refined anisotropically. Hydrogen atom of the N3 atom is taken from a difference Fourier map and fixed its thermal parameter, while the other hydrogen atoms were in calculated positions using the riding method with $U_{\text{iso}}(\text{H})=1.2 U_{\text{eq}}(\text{C})$. Hydrogen bond and molecular packing geometry of the title molecule was calculated with PLATON [11]. The graphical representations of the structure were made with ORTEP [12] (see Fig. 2) and MERCURY [13]. The crystal and instrumental parameters used in the unit cell determination and data collection are summarized in Table 3. Selected bond lengths and angles are given in Table 4. ORTEP drawing of the molecule with 20% probability displacement thermal ellipsoids and atom-labeling scheme are shown in Fig. (2).

CONCLUSION

The molecule of the title compound has $\text{C}=\text{N}$ and $\text{N}=\text{N}$ double bond [$\text{C}13-\text{N}4=1.324(10)$, $\text{N}1-\text{N}2=1.300(10)$ Å]. The exocyclic $\text{C}-\text{C}-\text{N}$ bond angles around the C1 atom are asymmetrical. The $\text{C}6-\text{C}1-\text{N}1$ angle [$111.2(8)^\circ$] is significantly smaller than the $\text{C}2-\text{C}1-\text{N}1$ angle [$128.2(8)^\circ$]. $\text{C}13-\text{N}2-\text{N}1$ [$122.7(9)^\circ$] and $\text{C}13-\text{N}4-\text{N}3$ [$121.0(8)^\circ$] angles around the N2, N4 atoms are almost equal to each other. The aromatic rings in the molecule as expected have usual bond lengths and angles. The title compound has a strong intramolecular $\text{N}3-\text{H}\cdots\text{N}1$ hydrogen bond with $\text{D}-\text{H}$, $\text{D}\cdots\text{A}$ and $\text{H}\cdots\text{A}$ distances of 0.96(5), 2.405(11) and 1.59(6) Å, respectively, and $\text{D}-\text{H}\cdots\text{A}$ angle of $140(8)^\circ$ as shown Fig. (3a). This bond turns the molecule in to a chelate structure, which is responsible for its tautomerism. This hydrogen bond possibly influences the relative orientation of the phenyl rings. Tautomerism of 1,3,5 triphenylformazan was also seen

Table 1. The IR Data of 1-(p-Bromophenyl)-3,5 Diphenylformazan (in KBr, cm^{-1})

Aromatic C-H	Aromatic C=C	C=N	N=N	N-N Valans Vibration	CNNC Structural Vibration
3100	1605	1520 1500	1450 1410	1080 1055 1030	935-840

Table 2. UV- visible Absorption Maxima of Formazans (CH_3OH , 10^{-4}mol/l)

Compound	$\lambda_{\text{max}1}$ (nm)	$\lambda_{\text{max}2}$ (nm)	$\lambda_{\text{max}3}$ (nm)	$\Delta \lambda_{\text{max}}$ (nm)	σ
1, 3, 5 triphenylformazan (TPF)	483	335	298	-	-
1-(p-bromophenyl)-3,5 diphenylformazan	489	300	230	7	0.23

$\Delta \lambda_{\text{max}} = \lambda_{\text{max}1}(\text{TPF}) - \lambda_{\text{max}1}(\text{substituted formazan})$.

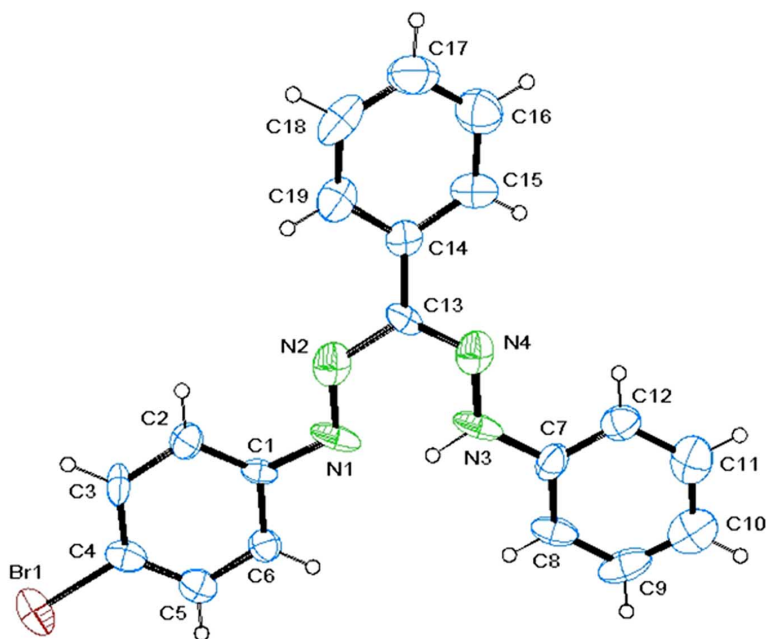


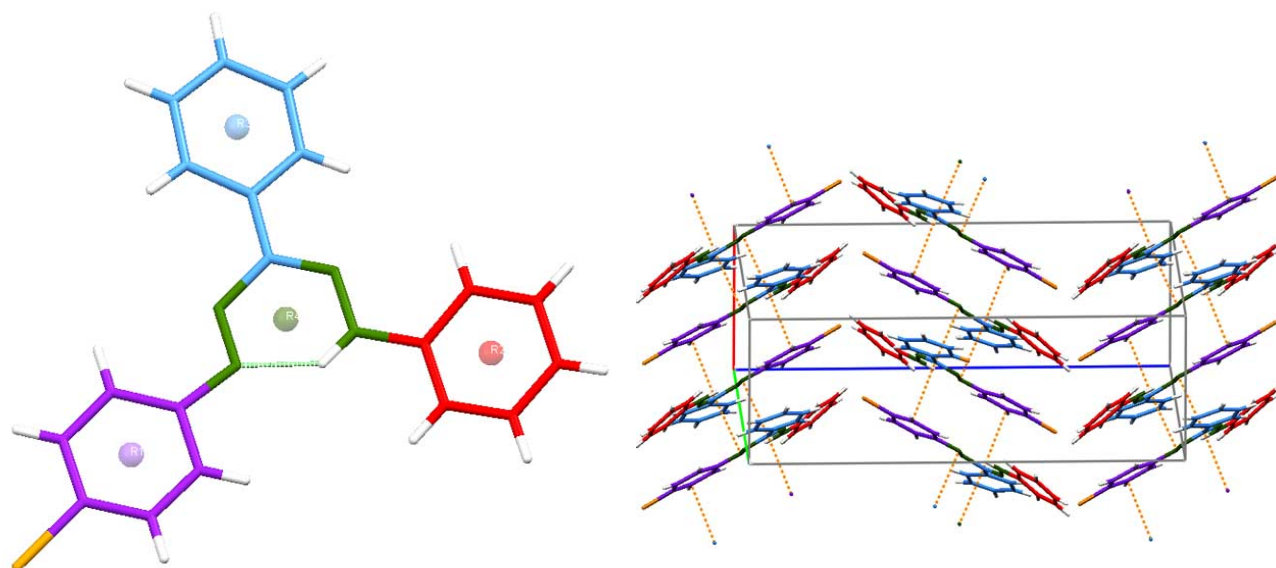
Fig. (2). ORTEP drawing of the title compounds with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 3. Crystal Data and Structure Refinement Details for Complex

Formula	$C_{19}H_{15}BrN_4$
Formula weight [g/mol]	379.25
Crystal system / space group	orthorhombic / $Pbc a$
Unit cell dimensions: [Å]	$a = 7.9526(9)$, $b = 18.611(2)$, $c = 23.099(3)$
Cell volume [Å ³] / Z	3418.8(7) / 8
Calculated density [g/cm ³]	1.474
Crystal colour / shape / size [mm]	Red / needle / 0.50 x 0.04 x 0.04
$F(000)$	1536
Absorption coefficient [mm ⁻¹]	2.412
Absorption correction type	Integration
T_{max} / T_{min}	0.890 / 0.923
θ -range for data collection [°]	1.76 – 26.00
Limiting indices	$0 \leq h \leq 9$, $0 \leq k \leq 22$, $0 \leq l \leq 28$
Reflections collected / Unique	23082 / 3353
Data / parameters / restraints	3353 / 220 / 2
Goodness-of-fit on F^2	0.864
wR	0.124
Final R indices [$I > 2\sigma(I)$]	0.0703
Max. & min diff. peak and hole [e/Å ³]	0.449 & -0.237

Table 4. Selected Bond Lengths and Angles (Å,°)

Br1 – C4	1.890(8)	N1 – N2 – C1	110.8(10)	N3 – C7 – C12	119.0(10)
N1 – N2	1.300(10)	N1 – N2 – C13	122.7(9)	N4 – N3 – H	116(5)
N1 – C1	1.450(10)	N4 – N3 – C7	120.8(8)	N3 – H ... N1	140(8)
N2 – C13	1.475(11)	N3 – N4 – C13	121.0(8)	Br1 – C4 – C3	119.7(8)
N3 – N4	1.373(9)	N2 – C13 – N4	117.1(10)	Br1 – C4 – C5	120.5(8)
N3 – C7	1.415(11)	N2 – C13 – C14	126.9(9)		
N3 – H	0.96(5)	N4 – C13 – C14	116.1(8)	N3 – N4 – C13 – N2	2.6(10)
N4 – C13	1.324(10)	N3 – C7 – C8	120.4(10)	N1 – N2 – C13 – N4	1.9(11)

**Fig. (3).** (a) View of the center of rings in compound, (b) View of the crystal packing.

before in spectral investigation [3]. The molecule has almost planar conformation. In the asymmetric unit of the molecule, the dihedral angle between the least square planes of the phenyl rings R1 [C1-C2-C3-C4-C5-C6], R2 [C7-C8-C9-C10-C11-C12], R3 [C14-C15-C16-C17-C18-C19] and the chelate ring R4 [N1-N2-C13-N4-N3-H] are given in Table 5 (see Fig. 3a). In the crystal structure, the shortest intermolecular π -ring distance of 4.135(6) Å is observed between R1 and R3ⁱ (symmetry codes i: 1-x,-y,-z). In addition to this, there exist weak intermolecular interactions between N1-C13ⁱ and C5-C13ⁱⁱ. The distances are 3.210(11) and 3.369(11) Å, respectively (symmetry codes i: 1-x,-y,-z ii: 2-x,-y,-z). The molecules in the crystal structure are stacked along the a-axis as shown Fig. (3b).

Table 5. Dihedral Angles Between the Least-Squares Planes of Rings

Ring No	Ring No	Dihedral Angle (°)
R1	R2	12.36
R1	R3	12.13
R1	R4	2.98
R2	R3	23.92
R2	R4	10.51
R3	R4	14.95

APPENDIX A. SUPPLEMENTARY DATA

CCDC contains the supplementary crystallographic data 742262. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Received: January 08, 2010

Revised: February 01, 2010

Accepted: February 04, 2010

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