Chapter

X-Ray Crystal Structure Analysis of Selected Benzimidazole Derivatives

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Abstract

This chapter describes the X-ray crystal structure analysis of selected benzimidazole derivatives, viz. BIP: 2-(1H-benzimidazol-2-yl)phenol, MBMPBI: 1-(4-methylbenzyl)-2-(4-methylphenyl)-1H-benzimidazole, DPBI: 1,2-diphenyl-1H-benzimidazole, PBIP: 2-(1-phenyl-1H-benzimidazol-2-yl)phenol, FPPBI: 2-(4-fluorophenyl)-1-phenyl-1H-benzimidazole and NPBIBHS: 2-(naphthalen-1-yl)-1-phenyl-1H-benzimidazole benzene hemisolvate. The BIP molecule is planar, and in the crystal, it is arranged in parallel planes, stabilised by π-π interactions and the hydrogen bonds. In MBMPBI, benzimidazole cores of the two independent (A and B) molecules are planar. Two C—H...N hydrogen bonds link B molecules only, forming centrosymmetric dimers with $R^2_2(8)$ ring motifs. In the DPBI molecule, the benzimidazole core is planar: one hydrogen-bond interaction (C—H...N) and C—H...π (three) interaction leading to the three-dimensional arrangement. In the PBIP molecule, the benzimidazole is nearly planar. The hydrogen bonds and a π-π stacking interaction are present in the crystal. In the FPPBI molecule, the benzimidazole unit is almost planar. The C—H...F hydrogen bonds and weak C—H...π interactions lead to a three-dimensional architecture in the crystal. In NPBIBHS, the naphthalene fragment lies out of the plane about the benzimidazole core unit. The C—H...N hydrogen bonds and C—H...π interactions lead to a three-dimensional architecture in the crystal.

Keywords: X-ray, single crystal, synthesis, structural analysis, inter and intramolecular hydrogen bonds, C—H...π and π...π interactions

1. Introduction

The X-ray diffraction technique is the most powerful technique of determining the relative atomic positions in a molecular structure. Furthermore, it is distinctively capable of providing precise evidence concerning bond lengths, bond angles, torsion angles and molecular dimensions. It is a well-known fact that hydrogen bonding is one of the crucial factors that contribute to the stability of a structure. Thus, it forms a part of the molecular conformation in that the symmetry and the subsequent packing of the molecules should yield the formation of as many hydrogen bonds as possible. This present chapter depicts the work carried out by the authors, on the crystal structure determination of selected biologically important new benzimidazole derivatives.

Literature survey shows that the benzimidazole is an aromatic ring system where an imidazole ring is fused to the 4 and 5 positions with a benzene ring. Benzimidazole derivatives in OLEDs are of current interest because of their thermal stability [1]. Benzimidazole derivatives are a part of vitamin B_{12} [2] and commercialised as anthelmintic and antihistaminic agents [3].

2. Synthetic approaches of benzimidazole compounds

Due to their possible biological and pharmacological activities, benzimidazoles synthesis has become a vital target in recent years [4]. Since our group is researching organic light emitting devices (OLEDs), we are concerned in using the MBMPBI [5] and DPBI [6] compounds as a ligand in the preparation of Ir(III) complexes and exploring further their electroluminescence (EL) properties. Furthermore, we are interested in using the PBIP [7], FPPBI [8] and NPBIBHS [9] compound as a ligand to study excited state intramolecular proton transfer (ESIPT) processes.

2.1 Synthesis of 2-(1H-benzimidazol-2-yl)phenol ($C_{13}H_{10}N_2O$): BIP

To 15 mmol of o-phenylenediamine in minimum 10 ml ethanol, a mixture of 15 mmol of o-hydroxybenzaldehyde and 60 mmol of ammonium acetate was added and refluxed at 90°C for 2 days. The reaction mixture was cooled and extracted with dichloromethane. The TLC monitored the completion of the reaction. The separated solid was purified by column chromatography (benzene: ethyl acetate (9:1)), after solvent evaporation, and the yield was 60% (**Figure 1**). Furthermore, a suitable single crystal is subjected to collect the X-ray diffraction data [4].

2.2 Synthesis of 1-(4-methylbenzyl)-2-(4-methylphenyl)-1H-benzimidazole ($C_{22}H_{20}N_2$): MBMPBI

To 15 mmol of o-phenylenediamine in minimum 10 ml ethanol, a mixture of 15 mmol of p-methylbenzaldehyde and 60 mmol of ammonium acetate was added and refluxed at 90°C (48 h). Purification of MBMPBI was made by following the procedure as that of BIP (column chromatography: benzene: ethyl acetate (9:1)), and the yield was 40% (**Figure 1**). Furthermore, a suitable single crystal is subjected to collect the X-ray diffraction data [5].

2.3 Synthesis of 1,2-diphenyl-1H-benzimidazole ($C_{19}H_{14}N_2$): DPBI

To 17 mmol of N-phenyl-o-phenylenediamine in minimum 10 ml ethanol, a mixture of 17 mmol of benzaldehyde and 60 mmol of ammonium acetate was added and refluxed at 90°C (4 h). Purification of DPBI was made by following the procedure as that of BIP (column chromatography: benzene: ethyl acetate (9:1)), and the yield was 50% (**Figure 1**). Furthermore, a suitable single crystal is subjected to collect the X-ray diffraction data [6].

2.4 Synthesis of 2-(1-phenyl-1H-benzimidazol-2-yl)phenol ($C_{19}H_{14}N_2O$): PBIP

To 17 mmol of N-phenyl-o-phenylenediamine in minimum 10 ml ethanol, a mixture of 17 mmol of o-hydroxybenzaldehyde and 60 mmol of ammonium acetate was added and refluxed at 90°C (4 h). Purification of PBIP was made by following

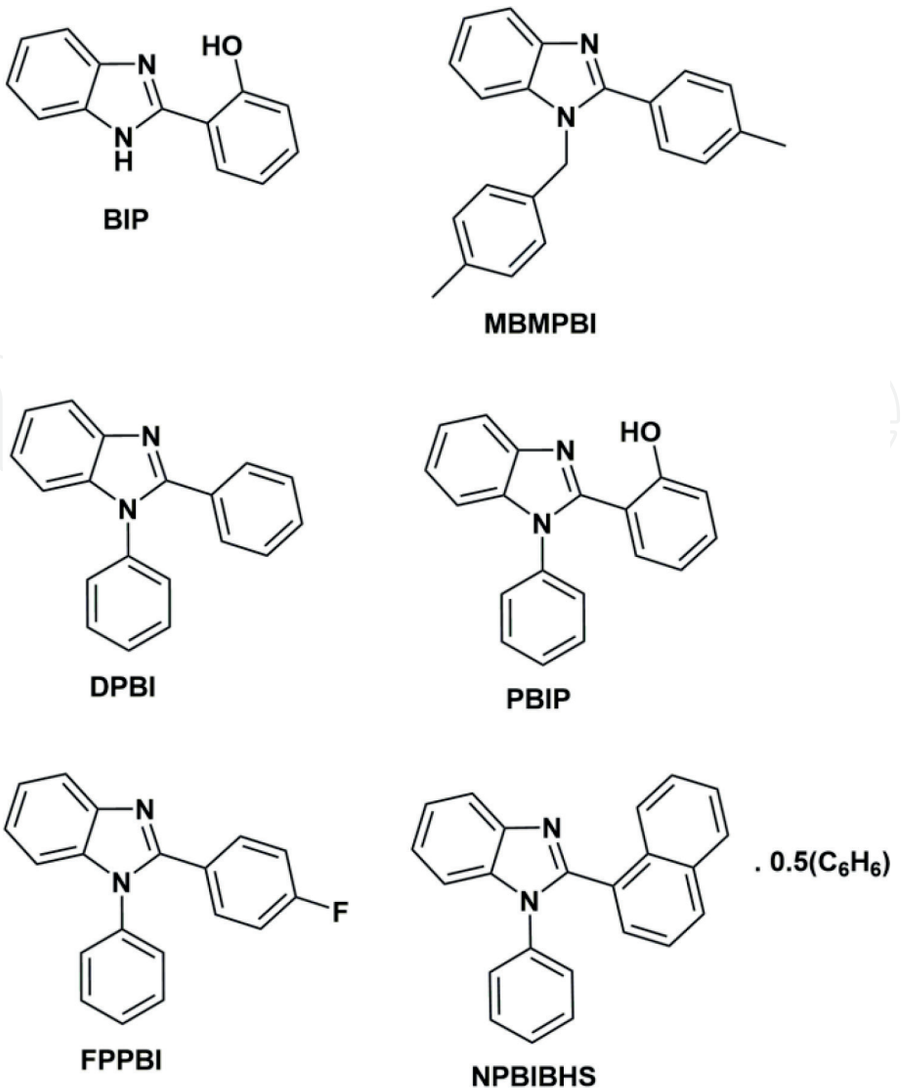

Figure 1.
Chemical structures of the studied compounds: BIP, MBMPBI, DPBI, PBIP, FPPBI and NPBIBHS.

the procedure as that of BIP (column chromatography-petroleum ether (60–80°C)), and the yield was 50% (**Figure 1**). Furthermore, a suitable single crystal is subjected to collect the X-ray diffraction data [7].

2.5 Synthesis of 2-(4-fluorophenyl)-1-phenyl-1H-benzimidazole ($C_{19}H_{13}FN_2$): FPPBI

To 17 mmol of N-phenyl-o-phenylenediamine in minimum 10 ml ethanol, a mixture of p-fluorobenzaldehyde (17 mmol) and 60 mmol of ammonium acetate was added and refluxed at 90°C (4 h). Purification of FPPBI was made by following the procedure as that of BIP (column chromatography-petroleum ether: ethyl acetate (9:1)), the yield was 50% (**Figure 1**). Furthermore, a suitable single crystal is subjected to collect the X-ray diffraction data [8].

2.6 Synthesis of 2-(naphthalen-1-yl)-1-phenyl-1H-benzimidazole benzene hemisolvate ($C_{23}H_{16}N_2$. $0.5C_6H_6$): NPBIBHS

To 17 mmol of N-phenyl-o-phenylenediamine in minimum 10 ml ethanol, a mixture of 17 mmol of 1-naphthaldehyde and 60 mmol of ammonium acetate was added and refluxed at 90°C (48 h). Purification of NPBIBHS was made by following

the procedure as that of BIP (column chromatography-benzene as the eluent), and the yield was 50% (**Figure 1**). Furthermore, a suitable single crystal is subjected to collect the X-ray diffraction data [9].

3. Structural analysis of six benzimidazole compounds

3.1 Structural analysis of 2-(1H-benzimidazol-2-yl)phenol (BIP)

This section describes the determination of the crystal structure and molecular structure of BIP [4]. The direct method program SIR2011 [10] is used in solving the crystal structure. The SHELXL2013/4 [11] program was used to refine the structure.

This compound crystallises in the monoclinic system in the space group $P2_1/c$. Molecular formula: $C_{13}H_{10}N_2O$; molecular weight: 210.23; Z = 4; crystal data: a = 16.864(4) Å; b = 4.7431(8) Å; c = 12.952(2) Å; β = 102.34(2)°; V = 1012.1(3) $Å^3$; D_{cal} = 1.380 Mg m^{-3}; F_{000} = 440; final R[$F^2 > 2\sigma(F^2)$] = 0.067 and wR(F^2) = 0.131 for 1184 reflections observed with $I > 2\sigma(I)$.

From a difference Fourier map, H_1 attached to N_1 was located and freely refined with (N_1—H_1 = 0.91(2) Å). The outstanding H atoms were placed geometrically and permitted to ride on their parental atoms, with O—H = 0.82 and C—H = 0.93 Å for Csp^2 hydrogens; $U_{iso}(H) = kU_{eq}(C)$, where k = 1.5 for methyl and 1.2 for all other C-bonded H atoms.

This molecule is planar [maximum deviation = 0.016(2) Å]. The dihedral angle between the five-membered imidazole ring and the attached six-membered benzene ring is 0.37(13)°. An S(6) ring motif [12] is generated by the O—H...N hydrogen bond. The hydrogen bond involves the hydroxyl substituent (O_{26}) as the proton donor and the nitrogen (N_3) atom as the acceptor, which forms a six-membered ring. The N—H...O hydrogen bonds link the molecules, by making chains spreading in [001]. Four π-π assembling contacts concerning the five-membered ring, fused six-membered benzene ring and attached benzene ring system [The C_g-C_g distances increase from 3.6106(17) to 3.6668(17) Å].

The thermal displacement ellipsoid plot (**Figure 2**) at the 50% probability level was drawn using the program ORTEP-3 for Windows [13]. **Figure 3** presents the π-π interactions detected in the crystal structure, brought using the program PLATON [14]. The crystal structure packing view is shown in **Figure 4** [14].

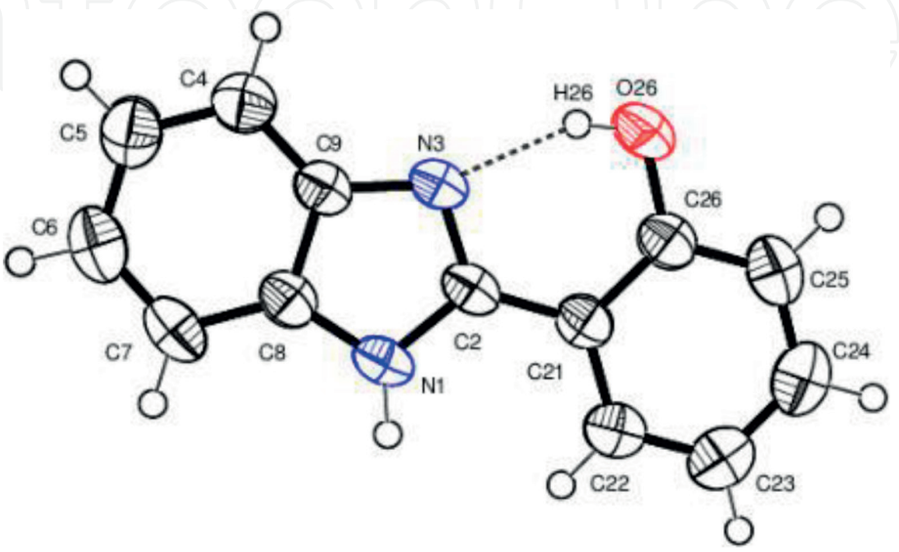

Figure 2.
The thermal displacement ellipsoid plot (at the 50% probability level).

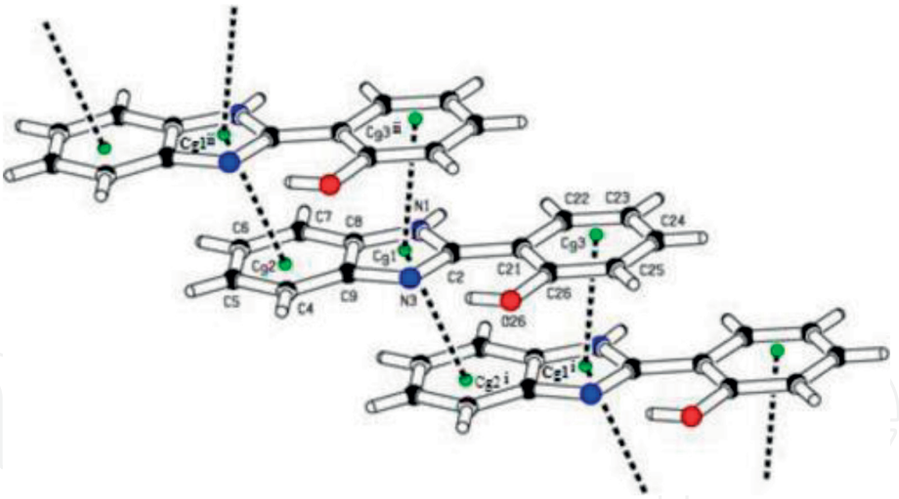

Figure 3.
The crystal structure, partially showing the formation of π-π interactions. Symmetry codes (i): x, −1 + y, z and (ii): x, 1 + y, z.

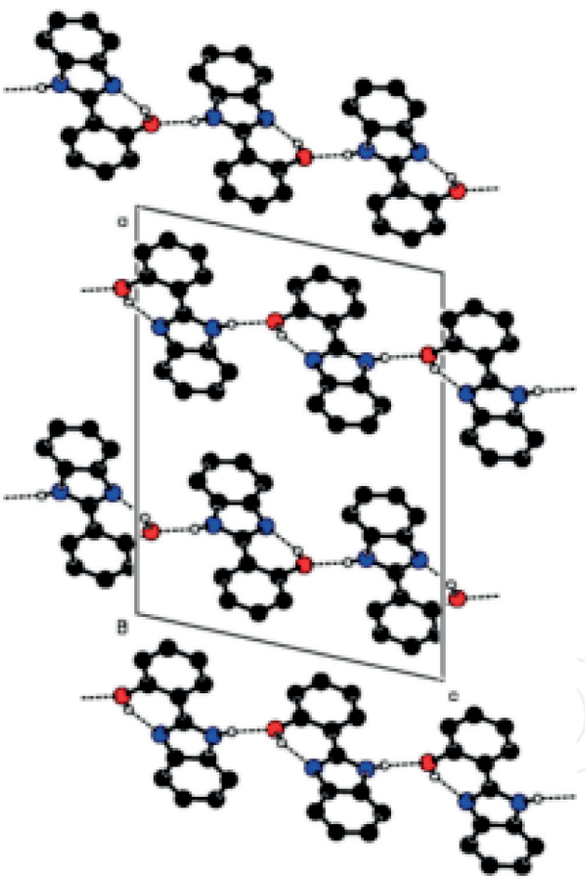

Figure 4.
The partial crystal packing with hydrogen bonds [14], viewed along the b axis.

3.2 Structural analysis of 1-(4-methylbenzyl)-2-(4-methylphenyl)-1H-benzimidazole (MBMPBI)

This section describes the determination of the crystal and molecular structure of MBMPBI [5]. The direct method program SIR2002 [15] is used in solving the crystal structure. The SHELXL97 [11] program was used to refine the structure.

This compound crystallises in the triclinic system in the space group P$\bar{1}$. Molecular formula: $C_{22}H_{20}N_2$; molecular weight: 312.40; Z = 4; crystal data: a = 9.6610(2) Å;

b = 10.2900(2) Å; c = 17.7271(3) Å; α = 84.437(2)°; β = 81.536(2)°; γ = 76.165(2)°; V = 1689.02(6) Å^3; D_{cal} = 1.229 Mg m^{-3}; F_{000} = 664; final R[$F^2 > 2\sigma(F^2)$] = 0.039 and wR(F^2) = 0.104 for 6452 observed reflections with $I > 2\sigma(I)$.

All the H atoms were placed geometrically and allowed to trip on their parental atoms, with C—H = 0.93 (Csp^2), 0.96 (methyl) and 0.97 Å (methylene) hydrogen atoms. $U_{iso}(H) = kU_{eq}(C)$, with k = 1.5 (—CH_3 H atoms) and 1.2 (for carbon-attached H atoms). The —CH_3 groups are disordered over two positions. So, they are refined as idealised disordered methyl groups with identical occupancy of the two locations.

Two crystallographically independent molecules A (first) and B (second) of this compound make the asymmetric unit. The planar [maximum deviations = 0.0161(8) Å for A (first) and 0.0276(8) Å for B (second)] benzimidazole least-squares plane and the benzene least-squares planes of the 4-methylbenzyl and 4-methylphenyl groups make dihedral angles of 76.64(3) and 46.87(4)° in A (first). The similar values in B (second) are 86.31(2) and 39.14(4)°. The two benzene rings make the dihedral angle of 73.73(3)° in A (first) and 80.69(4)° in B (second). The variation in the dihedral angles may be due to the H—H repulsions. The centrosymmetric dimers with $R^2_2(8)$ ring motifs [12] are formed by the two C_4B—H_4B...N_3B hydrogen bonds in B (second). The pattern contains a total of eight atoms in which two of them are donors, and two are acceptors, hence designated as $R^2_2(8)$. There are no corresponding interactions involving the A molecules.

The thermal displacement ellipsoid plot (for molecule A (first) only) (**Figure 5**) at the 30% probability level was drawn using the program ORTEP-3 for Windows [13]. The crystal structure packing view is shown in **Figure 6** [14].

3.3 Structural analysis of 1,2-diphenyl-1H-benzimidazole (DPBI)

This section describes the determination of the crystal structure and molecular structure of DPBI [6]. The direct method program SHELXS97 [11] is used in solving the crystal structure. The SHELXL97 [11] program was used to refine the structure.

This compound crystallises in the monoclinic system in the space group C2/c. Molecular formula: $C_{19}H_{14}N_2$; molecular weight: 270.32; Z = 8; crystal

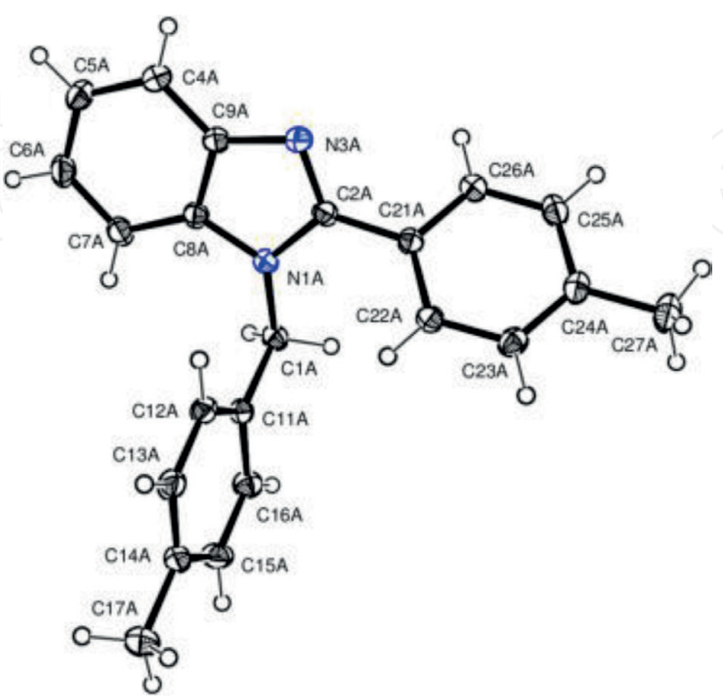

Figure 5.
The thermal displacement ellipsoid plot (at the 30% probability level).

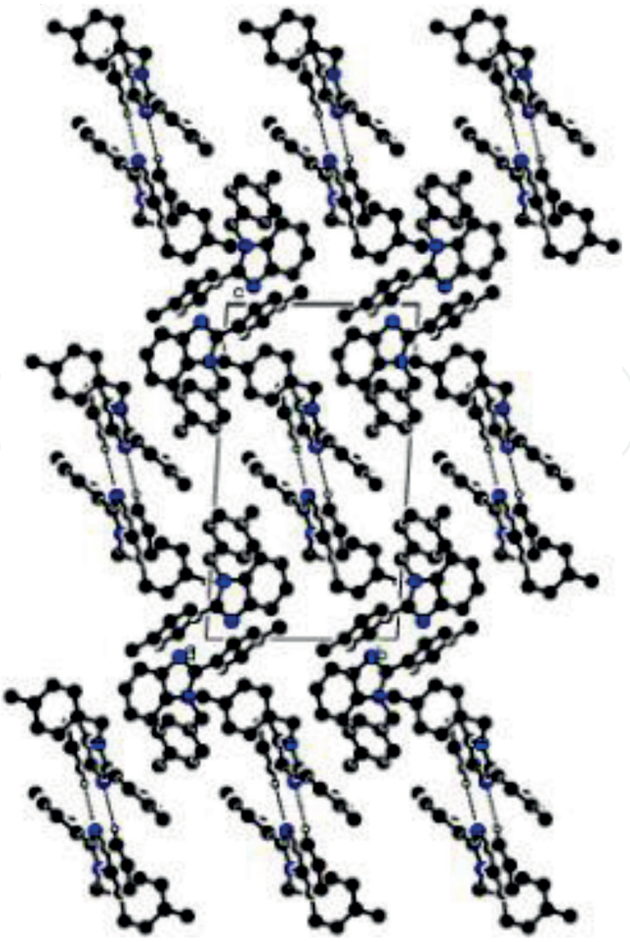

Figure 6.
The crystal packing with hydrogen bonds [14], viewed along the a axis.

data: a = 10.1878(3) Å; b = 16.6399(4) Å; c = 17.4959(5) Å; β = 106.205(3)°; V = 2848.13(14) Å^3; D_{cal} = 1.261 Mg m^{-3}; F_{000} = 1136; final R[$F^2 > 2\sigma(F^2)$] = 0.052 and wR(F^2) = 0.137 for 5803 reflections observed [$I > 2\sigma(I)$].

All the H atoms were placed geometrically and permitted to trip on their parental atoms, with C—H = 0.93 Å (Csp^2) and $U_{iso}(H) = kU_{eq}(C)$, where k = 1.5 for —CH_3 H atoms and 1.2 for all other H atoms.

The benzimidazole unit is planar [maximum deviation = 0.0102(6) Å]. The least-squares planes of the phenyl rings at N_1 and C_2 make angles of 55.80(2) and 40.67(3)° with the least-squares plane of the benzimidazole part. The least-squares planes of the phenyl rings at N_1 and C_2 make a dihedral angle of 62.37(3)°. One C—H...N hydrogen bond and three C—H...π interactions concerning the fused benzene ring and the five-membered imidazole rings are observed, forming a three-dimensional architecture in the crystal.

The thermal displacement ellipsoid plot (**Figure 7**) at the 50% probability level was drawn using the program ORTEP-3 for Windows [13]. **Figure 8** presents the C—H...π interactions in the crystal structure brought using the program PLATON [14]. The crystal structure packing view is shown in **Figure 9** [14].

3.4 Structural analysis of 2-(1-phenyl-1H-benzimidazol-2-yl)phenol (PBIP)

This section describes the determination of the crystal structure and molecular structure of PBIP [7]. The direct method program SHELXS86 [11] is used in solving the crystal structure. The SHELXL97 [11] program was used to refine the structure.

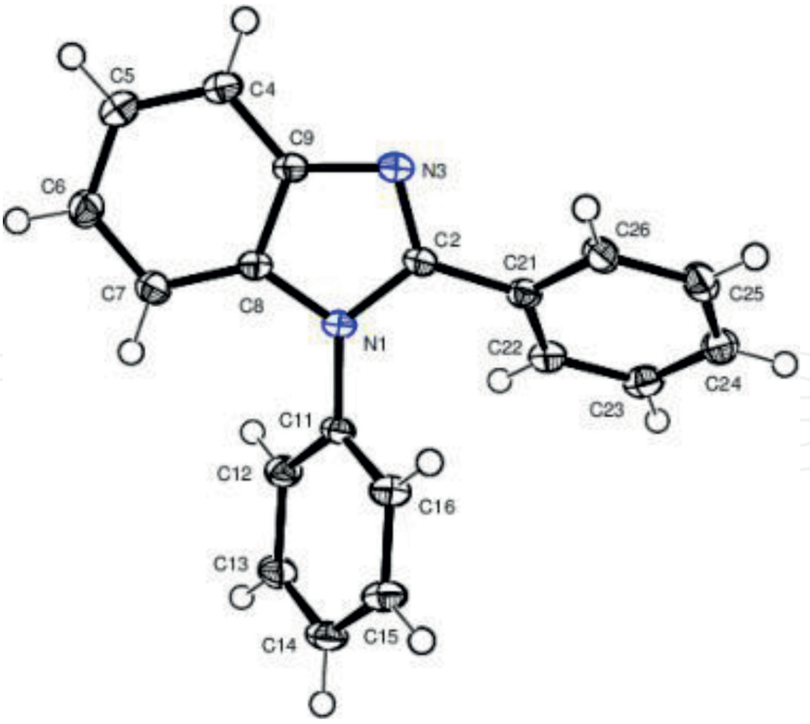

Figure 7.
The thermal displacement ellipsoid plot (at the 50% probability level).

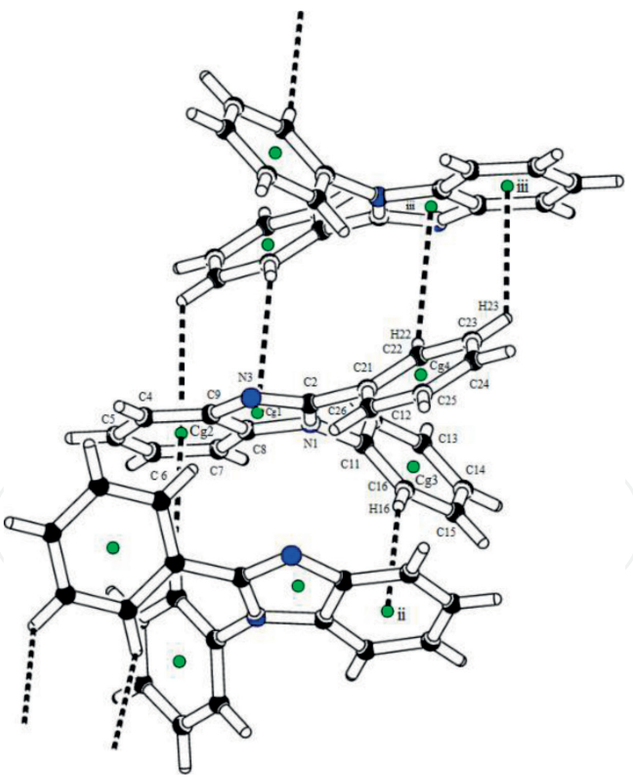

Figure 8.
The crystal structure, partially showing the formation of C—H…π interactions. Symmetry codes are (ii): –x, y, –z + 1/2 and (iii): –x, –y + 1, –z.

This compound crystallises in the triclinic system in the space group $P\bar{1}$ Molecular formula: $C_{19}H_{14}N_2O$; molecular weight: 286.32; Z = 2; crystal data: a = 8.1941(6) Å; b = 9.5983(14) Å; c = 10.3193(18) Å; α = 64.637(16)°; β = 80.356(10)°; γ = 83.610(9)°; V = 722.3(2) Å^3; D_{cal} = 1.316 Mg m^{-3}; F_{000} = 300; final R[$F^2 > 2\sigma(F^2)$] = 0.059 and wR(F^2) = 0.171 for 2420 observed reflections with I > 2σ(I).

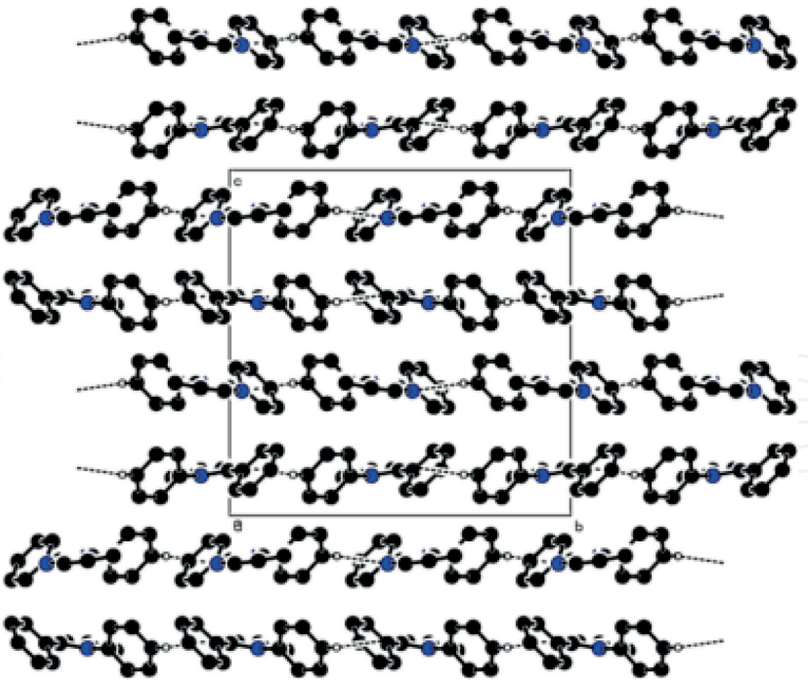

Figure 9.
The crystal packing with hydrogen bonds [14], viewed along the a axis.

A difference Fourier map was used to locate the H atom attached to O atom and refined freely with O_{26}—H_{26} = 0.97(3) Å. The outstanding H atoms were placed geometrically and permitted to trip on their parental atoms, with C—H = 0.95 Å, and with $U_{iso}(H) = 1.2U_{eq}$(parental atom).

The phenyl mean plane at N_1 and the benzene mean plane at C_2 makes angles of 68.98(6) and 20.38(7)°, respectively, with benzimidazole planar unit [maximum deviation = 0.0253(11) Å]. The phenyl and the adjacent benzene mean planes makes an angle of 64.30(7)°. An intramolecular S(6) ring motif [12] is generated by O—H...N hydrogen bond. The hydrogen bond involving has the hydroxyl substituent (O_{26}) as the proton donor and the nitrogen (N_3) atom as the acceptor, which forms a six-membered ring (N_3, C_2, C_{21}, C_{26}, O_{26} and H_{26}). The C—H...N and C—H...O hydrogen bonds links the molecules. There is a π-π assembling contact, with a centroid-centroid distance of 3.8428(12) Å.

The ORTEP-3 for Windows [13] was used to draw the thermal displacement ellipsoid plot (**Figure 10**) at the 50% probability level. **Figure 11** presents the π-π interactions observed in the crystal structure brought using the program PLATON [14]. The crystal structure packing view is shown in **Figure 12** [14].

The dashed lines indicate the intramolecular O—H...N hydrogen bond.

3.5 Structural analysis of 2-(4-fluorophenyl)-1-phenyl-1H-benzimidazole (FPPBI)

This section describes the determination of the crystal structure and molecular structure of FPPBI [8]. The crystal structure of FPPBI was solved by direct methods, using the program SIR2004 [16]. The crystal structure is refined by the program SHELXL97 [11].

This compound crystallises in the Monoclinic system in the space group $P2_1/n$. Molecular formula: $C_{19}H_{13}FN_2$; Molecular weight: 288.31; Z = 4; crystal data: a = 8.7527(4) Å; b = 10.1342(4) Å; c = 17.0211(6) Å; β = 104.187(4)°; V = 1463.75(11) $Å^3$; D_{cal} = 1.308 Mg m^{-3}; F_{000} = 600; final R[$F^2 > 2\sigma(F^2)$] = 0.063 and wR(F^2) = 0.160 for 5352 observed reflections with ($I > 2\sigma(I)$).

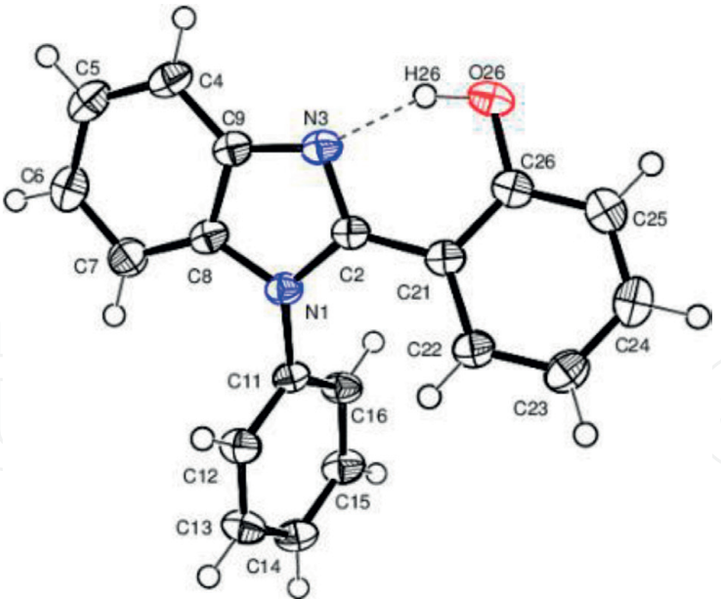

Figure 10.
The thermal displacement ellipsoid plot (at the 50% probability level).

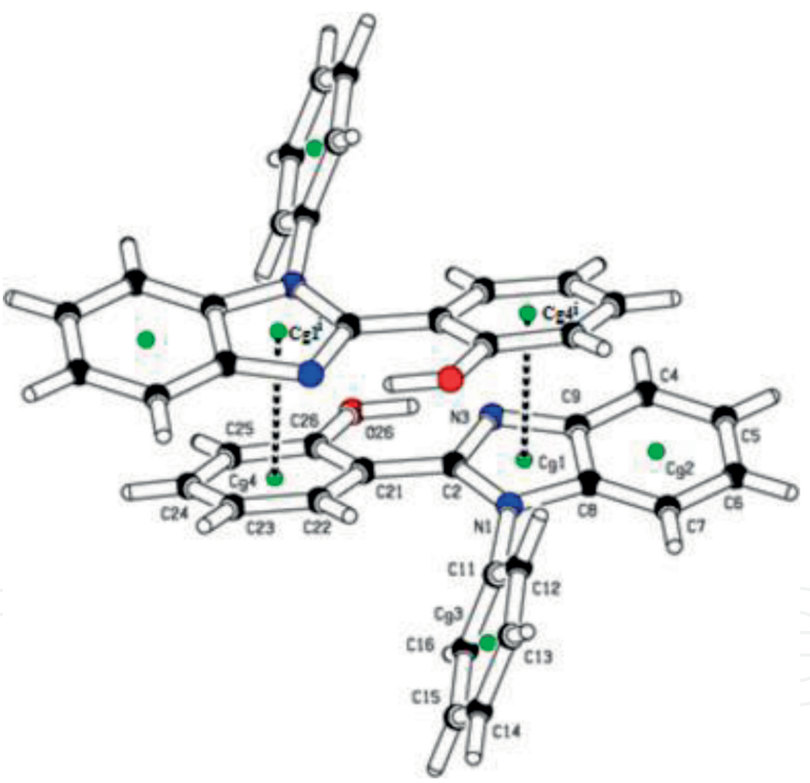

Figure 11.
The crystal structure, partially showing the formation of π-π stacking interactions. Symmetry code (i): 2 − x, −y, −z.

All the H atoms were placed geometrically and allowed to trip on their parental atoms, with C—H = 0.93 Å (Csp^2). $U_{iso}(H) = kU_{eq}(C)$, where k = 1.5 (CH_3H) and 1.2 (for all other carbon-attached H atoms).

The benzimidazole group is nearly planar [maximum deviation = 0.0342(9) Å]. The mean planes of the phenyl at N_1 and fluorobenzene at C_2 make dihedral angles of 58.94(3) and 51.43(3)°, respectively, with the benzimidazole least-squares plane. The phenyl and fluorobenzene mean planes make an angle of 60.17(6)°. Finally, three C—H...F hydrogen bonds and two weak C—H...π contacts connecting the fused benzene ring lead to a three-dimensional construction.

The ORTEP-3 for Windows [13] was used to draw the thermal displacement ellipsoid plot (**Figure 13**) at the 50% probability level. **Figure 14** presents the C—H...π interactions observed in the crystal structure, brought using the program PLATON [14]. The crystal structure packing view is shown in **Figure 15** [14].

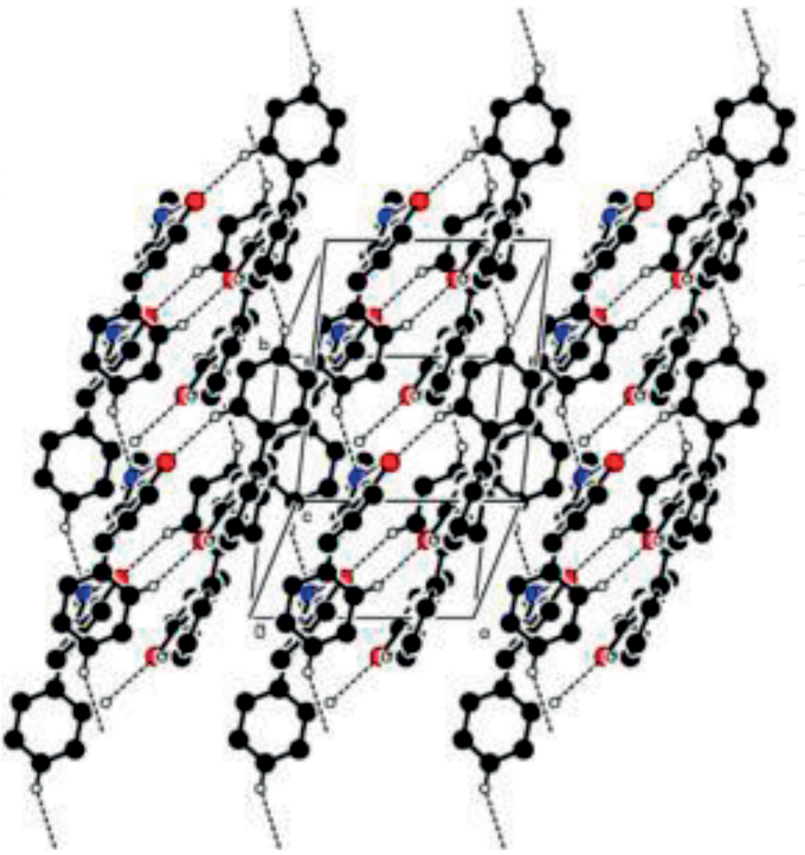

Figure 12.
The crystal packing with hydrogen bonds [14], viewed along the c axis.

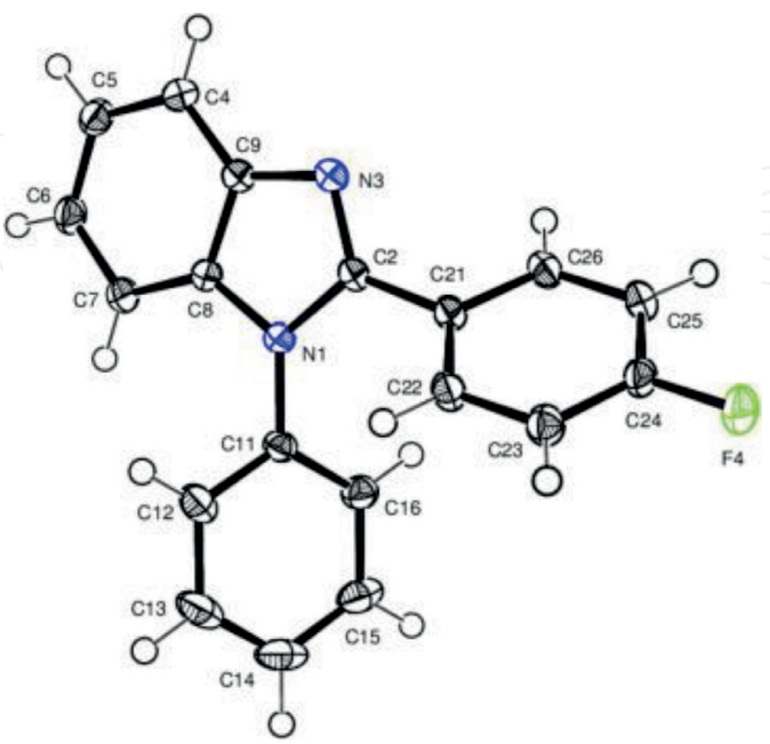

Figure 13.
The thermal displacement ellipsoid plot (at the 50% probability level).

3.6 Structural analysis of 2-(naphthalen-1-yl)-1-phenyl-1H-benzimidazole benzene hemisolvate (NPBIBHS)

This section describes the determination of the crystal structure and molecular structure of NPBIBHS [9]. The direct method program SHELXS2013 [11] was used to solve the crystal structure. SHELXL2013 [11] program is used to refine the crystal structure. This compound crystallises in the triclinic system in the space group $P\bar{1}$ Molecular formula: $C_{23}H_{16}N_2.0.5C_6H_6$; molecular weight: 359.43; Z = 2; crystal data: a = 8.5529(3) Å; b = 9.4517(3) Å; c = 11.8936(3) Å; α = 86.334(2)°;

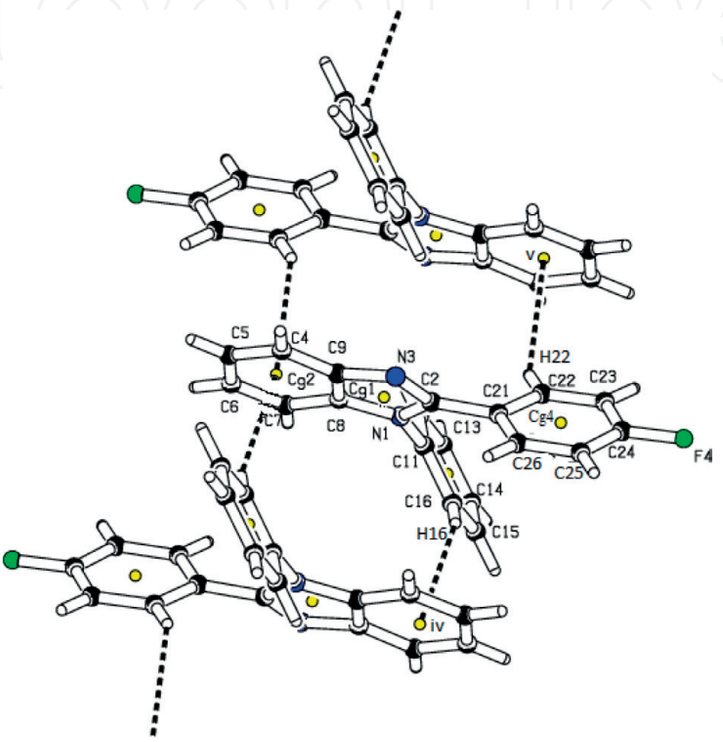

Figure 14.
The crystal structure, partially showing the formation of C—H…π interactions. Symmetry codes are (iv): −x, −y + 1, −z and (v): −x + 1, −y + 1, −z.

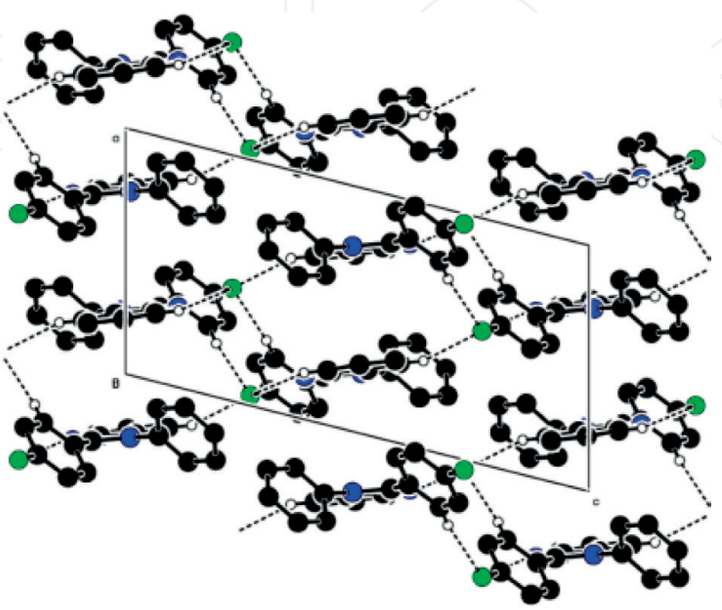

Figure 15.
The crystal packing with hydrogen bonds [14], viewed along the b axis.

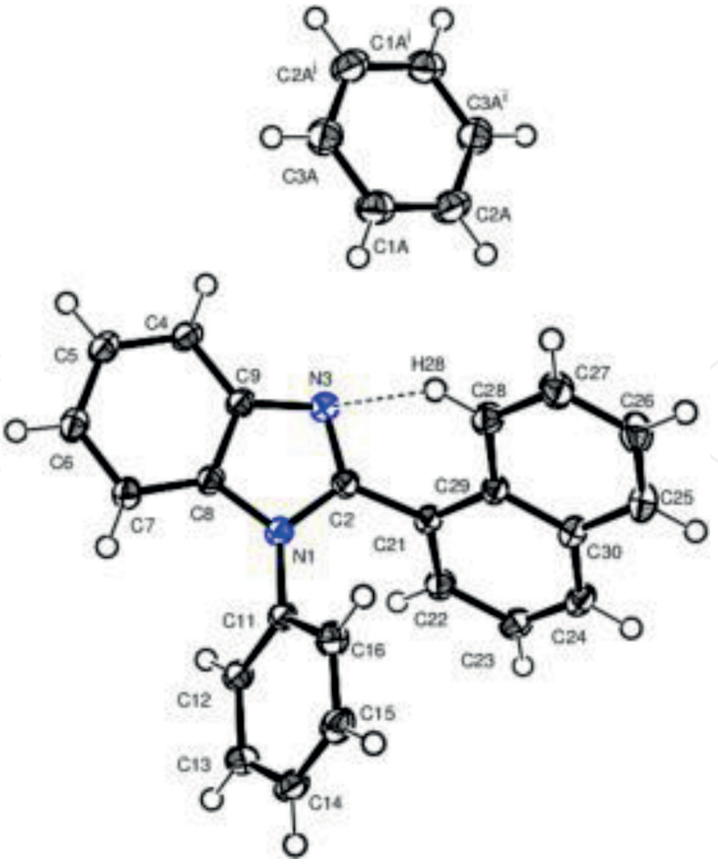

Figure 16.
The thermal displacement ellipsoid plot (at the 50% probability level).

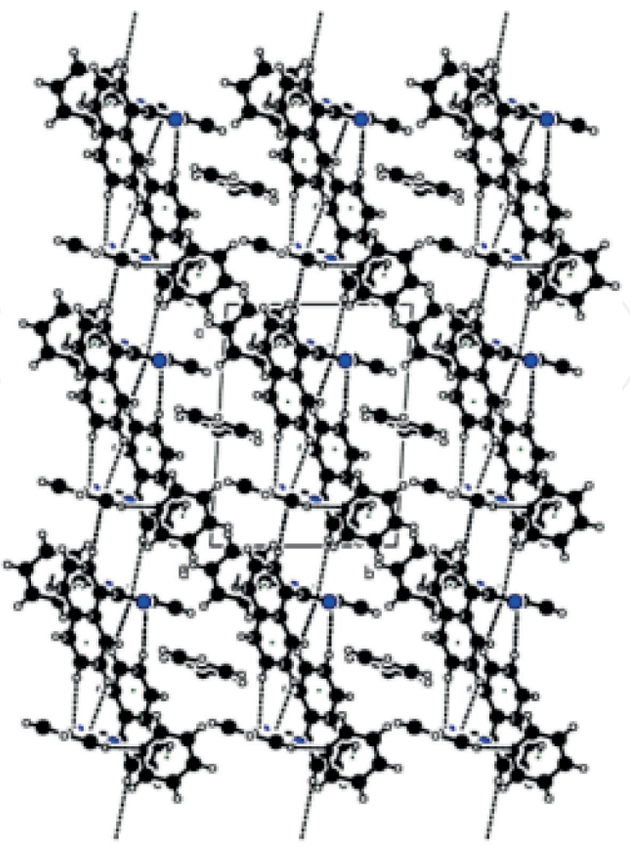

Figure 17.
The crystal structure, showing the formation of complex C—H…π interactions.

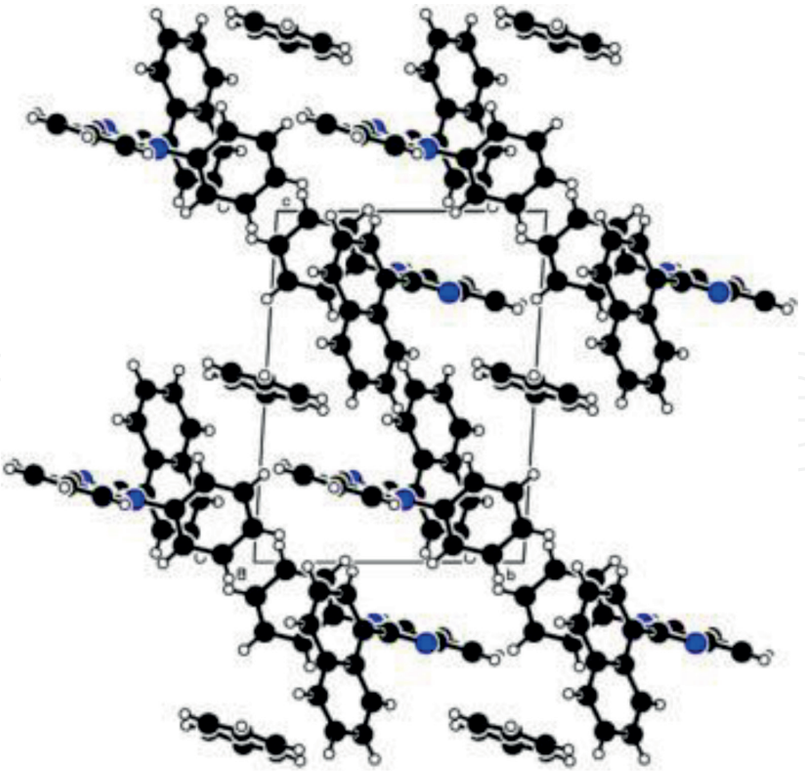

Figure 18.
The crystal packing with hydrogen bonds [14], viewed along the a axis.

β = 89.838(2)°; γ = 75.051(3)°; V = 926.94(5) Å^3; D_{cal} = 1.288 Mg m^{-3}; F_{000} = 378; final R[$F^2 > 2\sigma(F^2)$] = 0.057 and wR(F^2) = 0.160 for 9086 observed reflections with I > 2σ(I).

All the H atoms were placed geometrically and permitted to trip on their parental atoms, with C—H = 0.95 Å (Csp^2) and U_{iso}(H) = kU_{eq}(C), where k = 1.5 (—CH_3 H) and 1.2 (for all other H).

The benzimidazole least-squares plane [maximum deviation = 0.0258(6) Å] and the naphthalene least-squares plane [maximum deviation = 0.0254(6) Å] make dihedral angle of 61.955(17)°. The least-squares planes of the imidazole ring and the phenyl ring make a dihedral angle of 61.73(4)°. An intramolecular S(6) ring motif [12] is generated by the C—H...N hydrogen bond. The hydrogen bond involving has the carbon atom (C_{28}) as the proton donor and the nitrogen atom (N_3) as the acceptor, which forms a six-membered ring. Seven weak C—H...π links concerning the attached ring system, the benzene solvent molecule, the imidazole and the phenyl rings are detected, to a three-dimensional architecture.

The thermal displacement ellipsoid plot (**Figure 16**) at the 50% probability level was drawn using the program ORTEP-3 for Windows [13]. **Figure 17** presents the C—H...π interactions observed in the crystal structure brought using the program PLATON [14]. The crystal structure packing view is shown in **Figure 18** [14].

4. Comparative study on the structural aspects of the six benzimidazole derivatives

Section 3 presents the X-ray crystal structure analyses of six closely related organic benzimidazole compounds. The MBMPBI compound is similar to 2-(1H-benzimidazol-2-yl)phenol (BIP) except for the presence of methylbenzyl at the first position of the benzimidazole unit, a methyl at the fourth position of the phenyl group and the absence of hydroxyl group. The DPBI compound is similar to 2-(1H-benzimidazol-2-yl)phenol (BIP) except for the presence of a phenyl group at

the first position of the benzimidazole unit and the absence of an —OH group. The PBIP compound is similar to that of 2-(1H-benzimidazole-2-yl)phenol (BIP) except for the presence of a phenyl group at the first position of the benzimidazole unit and the absence of the —H atom. The FPPBI compound is like that of 1,2-diphenyl-1H-benzimidazole (DPBI) except for the presence of a fluorine atom at the fourth position of the phenyl group in the second location of the benzimidazole core.

All the six structures have the benzimidazole core essentially as the basic skeleton, with different groups (—H, —C_6H_4—OH, —CH_2—C_6H_4—CH_3, —C_6H_4—CH_3, —C_6H_5, —C_6H_5, —C_6H5, —C_6H_4—OH, —C_6H_5, —C_6H_4-F, —C_6H_5, and —$C_{10}H_7$) as substituents. The structural determinations of the compounds have revealed several features, such as (1) the hydrogen bonds: O—H…N, N—H…O, C—H…N, C—H…O, C—H…F; (2) interactions C—H…π and (3) stacking interactions π-π.

A type of hydrogen bond operational among a soft acid CH and a soft base π-system is known as a C—H…π interaction. The most striking contacts are (1) the connections among the aliphatic C—H donors and the aromatic π-acceptors and (2) the connections among the aromatic C—H donors and aromatic π-acceptors. The non-covalent contacts that encompass the π systems in chemistry are the π-effects or the π-interactions.

Related crystal structures: 1293 articles match the search term 'Benzimidazole' on IUCr Journals Crystallography Journals Online (https://journals.iucr.org/) as on February 10, 2019. The search (IUCr Journals' paper reference codes are: bh2413: 2-(4-chlorophenyl)-1-phenyl-1H-benzimidazole, bi2334: 1-benzyl-2-phenyl-1H-benzimidazole, bv2218: 1-phenyl-2-[4-(trifluoromethyl)phenyl]-1H-benzimidazole, bx2457: 1-(4-bromobenzyl)-2-(4-bromophenyl)-1H-benzimidazole, ci2926: 1-benzyl-1H-benzimidazole, fy2081: 1-phenyl-2-p-tolyl-1H-benzimidazole, go2077: 2-(4-methoxyphenyl)-1-phenyl-1H-benzimidazole, hk2704: 2-p-tolyl-1-p-tolylmethyl-1H-benzimidazole, lh5659: 2-(3,4-difluorophenyl)-1H-benzimidazole and lh5706: 2-[4-(trifluoromethyl)phenyl]-1H-benzimidazole)) confirms that the geometry of the benzimidazole cores is similar in all the reported structures.

5. Conclusions

This chapter described the research work carried out by the authors on the crystal structure determination of some selected biologically important new benzimidazole derivatives by using X-rays. The detailed structural analyses on the bond lengths, bond angles, torsion angles and dihedral angles between the least-squares planes of these six benzimidazole derivatives indicate that in the compounds BIP, MBMPBI, DPBI, PBIP, FPPBI and NPBIBHS, the benzimidazole unit is essentially planar as expected and as revealed by the latest literature survey (https://journals.iucr.org/). The present X-ray study confirms that the benzimidazole skeleton has an imidazole planer five-membered heterocyclic ring fused with the benzene ring. The basic geometrical examination (bond lengths and bond angles) of the benzimidazole core in the BIP molecule are in good agreement with those observed in other closely related benzimidazole derivatives. All the substituents are in the expected positions around the benzimidazole units. The X-ray study confirms the molecular structure and atom connectivity of the above-studied compounds as shown in **Figures 2**, **5**, **7**, **10**, **13** and **16**. The O—H…N, N—H…O, C—H…N, C—H…O, C—H…F hydrogen bonds, C—H…π and the π-π interactions are effective in the stabilisation of the crystal structure. We are interested in studying the biological and photophysical properties of BIP, MBMPBI, DPBI, PBIP, FPPBI and NPBIBHS compounds. The benzimidazole derivatives are a sensitive fluorescent sensor for TiO_2 (P_{25}), Fe_2O_3, WO_3, Al_2O_3,

CuO, TiO_2 (H), ZnO, Cu-ZnO, Ag-ZnO, TiO_2 (R) and TiO_2 (A) nanoparticles. The benzimidazole-based iridium(III) complexes show green emission with maximum electroluminescent efficiencies at low voltage.

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Conflict of interest

There is no conflict of interest in writing this chapter.

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List of abbreviations (a partial crystallographic information file (CIF) for the compound BIB only as an example)

_space_group_crystal_system	monoclinic
_space_group_name_H-M_alt	P 2_1/c
_chemical_formula_moiety	C13 H10 N2 O
_chemical_formula_weight	210.23
_cell_formula_units_Z	4
_cell_length_a	16.864(4)
_cell_length_b	4.7431(8)
_cell_length_c	12.952(2)
_cell_angle_alpha	90
_cell_angle_beta	102.34(2)
_cell_angle_gamma	90
_cell_volume	1012.1(3)
_exptl_crystal_density_diffrn	1.380
_exptl_crystal_F_000	440
_reflns_threshold_expression	I > 2(I)
_refine_ls_R_factor_gt	0.067
_refine_ls_wR_factor_gt	0.131
_reflns_number_gt	1184

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