

Synthesis and Crystal Structure of Charge Transfer Complex (CTC) of 2-Aminobenzothiazole with Its Schiff Base

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Abstract A novel charge transfer complex (CTC), $C_{14}H_{10}N_2OS \cdot C_7H_6N_2S$ was synthesized by the reaction of 2-aminobenzothiazole (ABT) with its derivative Schiff base (2-((benzo[d]thiazol-2-ylimino) methyl) phenol is abbreviated as BYMBP) in THF. This complex was characterized by 1H NMR, ^{13}C NMR, IR and UV-vis. Crystal structure of the complex has been determined by X-ray diffraction. The crystal is triclinic, space group P-1 with the unit cell parameters $a = 9.7732(5)$, $b = 9.9936(4)$, $c = 11.0193(7)$ Å and $\alpha = 71.901(9)$, $\beta = 78.686(10)$, $\gamma = 70.397(9)^\circ$, $Z = 2$, $R = 0.0499$. $wR_2 = 0.1190$. The structure of the title complex was fully optimized at the RB3LYP/6-311++g(d,p) level of theory and CTC's π - π stacking interaction, bond lengths (Å) and angles ($^\circ$) were calculated.

Keywords Charge transfer complexes · Schiff bases · X-ray diffraction · π - π Stacking · Theoretical calculations

Introduction

The arrangements of the molecules forming the packed arrays are controlled by the interplay of several different

weak intermolecular interactions: π - π stacking, C-H \cdots π and C-H \cdots N interactions, and these interactions bring about charge transfer. Charge transfer compounds are important components of optical material and have gradually been an active research area. Among these, D-A compounds exhibit particular optical properties because of their unique molecular structure, so they have been extensively investigated and widely used in luminescent, photoconductive, nonlinear optical material and so on [1–14]. Based on these features, more and more groups focus their research on charge transfer compounds, of which the ligands containing the conjugate systems of sulphur and nitrogen are widely studied currently. Amann had studied charge transfer complexes of Schiff bases derived from 2-aminobenzothiazole with some acidic and nonacidic acceptors [15]. Dumur et al. has reported Q-TTF-Q(1) and Q-TTF-Q(2), these complexes by themselves contain electron donor-acceptor (EDA) which leads to charge transfer [16]. Liu et al. have shown charge transfer complex TTF-TCNAQ [17]. These phenomena are originated from interaction between electron donor and acceptor molecules in biomolecular equilibrium or in model compounds with intramolecular interaction, which has been an important topic of research in physical chemistry and biochemistry for many decades [1–14]. So, syntheses of these complexes are always an attractive theme in the area of physical chemistry and biochemistry.

In this paper, synthesis and crystal structure of a new charge transfer complex was reported. In addition, the structural details of the complex have been investigated using RB3LYP/6-311++g(d,p) calculations [18]. In the gas phase, π - π stacking interaction, bond lengths (Å) and angles ($^\circ$) were calculated, and charge transfer (CT) can be seen in its molecule.

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Experimental

General

Melting points were determined in sealed argon-filled capillaries and uncorrected. Carbon, hydrogen, and nitrogen analyse were performed by direct combustion on a Carlo Erba-1110 instrument; quoted data are the average of at least two independent determinations. The IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr pellets. The single crystal X-ray diffraction data were recorded on a Rigaku Mercury CCD X-ray diffractometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Unity Inova-300 spectrometer. UV–vis spectra were recorded on a Shimadzu UV-3150 spectrometer. All calculations were carried out with the RB3LYP/6-311++g(d,p) [18].

Synthesis

Synthesis and Character of Schiff Bases (BYMBP)

2-Aminobenzthiazole (ABT): The aniline (0.1 mol) and ammonium thiocyanate (0.2 mol) in 150 mL of glacial acetic acid were cooled in an ice bath and stirred mechanically. To the solution, bromine (0.2 mol) in 25 mL of glacial acetic acid was added dropwise at such a rate to keep the temperature below 10 °C throughout the addition. Stirring was continued for additional thirty minutes after the bromine addition. The precipitate of the benzthiazole hydrobromide was collected, dissolved in hot water and basified with a saturated sodium carbonate solution. The free substituted benzthiazol was collected, washed with water and dried under vacuum. Recrystallization from the appropriate solvent gave 2-aminobenzthiazol in good yield (88.5%). m.p.: 129–130 °C. ^1H NMR (CDCl_3 , 300 MHz) (δ , ppm): 7.57–7.52 (m, 2 H, ArH), 7.29–7.12 (m, 2 H, ArH), 5.85 (brs, 2 H, $-\text{NH}_2$); ^{13}C NMR (CDCl_3 , 75 MHz) (δ , ppm): 166.4, 152.0, 131.5, 126.0, 122.2, 120.9, 119.0. IR (KBr, cm^{-1}): 3399(s), 3274(m), 3067(s), 2929(m), 1645(s), 1530(s), 1448(s), 1316(m), 1310(m), 1285(m), 1123(m), 1017(m), 920(m), 889(m), 741(s), 720(sh), 706(s), 687(m), 484(m).

Schiff bases (BTYMP): To a 10 mL EtOH solution of salicylaldehyde and a catalytic amount of formic acid was added a 5 mL EtOH solution of the appropriate amine (0.9 eq.). The mixture was refluxed for 8 h and the solution stored at 5 °C overnight. The resulting precipitate was collected by suction filtration and washed with Et_2O (3×10 mL). Yield: 85% of an orange solid, m.p.: 150–151 °C. ^1H NMR (CDCl_3 , 300 MHz) (δ , ppm): 12.24 (s, 1 H, OH), 9.26 (s, 1 H, CH=N), 7.98 (d, $J = 8.2$ Hz, 1 H, Ar), 7.84 (d, $J = 7.8$ Hz, 1 H, Ar), 7.52–7.45 (ov m, 3 H, Ar), 7.40–7.35 (m, 1 H, Ar), 7.06 (d, $J = 8.4$ Hz, 1 H, Ar),

7.01–6.97 (m, 1 H, Ar); ^{13}C NMR (CDCl_3 , 75 MHz) (δ , ppm): 169.2, 167.6, 162.2, 151.7, 135.6, 134.8, 134.3, 126.9, 125.5, 123.2, 122.0, 120.0, 118.5, 117.9. IR(KBr, cm^{-1}): 3300 (bs), 3055(s), 2949(s), 2873(s), 1606(v), 1570(vs), 1502(m), 1452(m), 1377(s), 1284(m), 1174(m), 1149(m), 1063(m), 901(s), 800(s), 754(s), 723(m), 679(m), 617(m).

Synthesis and Character of Charge Transfer Complex (CTC)

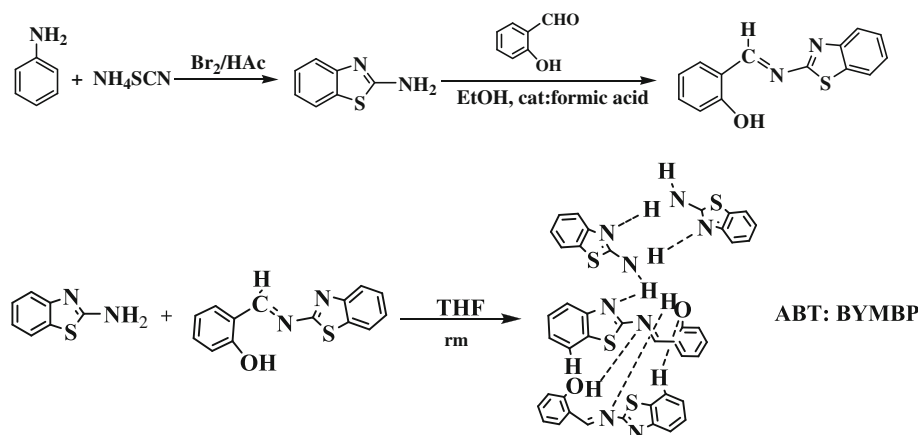
The CTC was prepared by mixing the equimolar amounts of BYMBP and ABT in THF at 60 °C for 8 h, during the time the pale yellow color changed gradually to yellow. The precipitate was removed from the reaction mixture by centrifugation, and THF was completely evaporated in vacuum, and ethanol was added to extract the product. Insoluble CTC was purified by being heated with ethanol several times to remove any contaminants, and the complex was filtered off, dried in vacuum. The crystal was grown from an ethanol-toluene mixture (1:10). Yellow microcrystals were obtained at room temperature in a few days, m.p.: 176–178 °C (dec). Anal. Calc. for $\text{C}_{21}\text{H}_{16}\text{N}_4\text{OS}_2$: C, 62.35; H, 3.99; N, 13.85; S, 15.85%. Found: C, 62.35; H, 3.99; N, 13.85; S, 15.85%. ^1H NMR (CDCl_3 , 300 MHz) (δ , ppm): 12.24 (s, 1 H, OH), 9.29 (s, 1 H, CH=N), 7.99 (d, $J = 8.2$ Hz, 1 H, Ar), 7.86 (d, $J = 7.8$ Hz, 1 H, Ar), 7.61–7.46 (ovm, 5 H, Ar), 7.38 (t, $J = 7.7$ Hz, 1 H, Ar), 7.32 (t, $J = 7.7$ Hz, 1 H, Ar), 7.14 (t, $J = 7.8$ Hz, 1 H, Ar), 7.07 (d, $J = 8.4$ Hz, 1 H, Ar), 7.01 (t, $J = 7.6$ Hz, 1 H, Ar), 5.25 (brs, 2 H, $-\text{NH}_2$); ^{13}C NMR (CDCl_3 , 75 MHz) (δ , ppm): 170.4, 167.6, 135.7, 134.3, 127.0, 126.2, 125.5, 123.2, 122.6, 122.0, 121.1, 120.1, 119.5, 118.6, 118.5, 117.9. IR(KBr, cm^{-1}): 3340(s,b), 3275(s,b), 3072(s), 2764(m), 2650(m), 1661(s), 1606(s), 1571(vs), 1541(s), 1501(s), 1478(s), 1448(s), 1316(m), 1288(s), 1255(m), 1239(m), 1182(s), 1149(s), 1123(m), 1064(m), 1017(m), 968(w), 931(w), 893(m), 889(s), 849(m), 788(m), 754(s), 724(s), 692(s).

Results and Discussion

Synthesis and Molecular Structure of the 1:1 Complex of ABT with BYMBP

BYMBP was prepared as described previously [15], and treated with 1 equiv of ABT in THF at 60 °C in order to prepare the corresponding 1:1 complex. The reaction went smoothly and after workup, the desired 1:1 complex was isolated in good yield as yellow crystals upon crystallization from toluene. Scheme 1 shows the reaction sequence.

The IR spectra of this complex exhibited the strong absorptions near 1571 and 1541 cm^{-1} indicating partial

Scheme 1 Synthesis of ABT:BYMBP complex

C=N double bond character [19]. This complex was further characterized by X-ray structure analysis. Figure 1 and 2 show the molecular structure and the packing of the title compound, respectively. The value of calculation and test of selected bond lengths and bond angles are given in Table 1. Single-crystal X-ray structure determination reveals that one unit cell of the title compound contains two independent molecules BYMBP and ABT in its crystals. From Fig. 2 we see a very interesting property of ABT:BYMBP: along the *b* axis, the nearby units connecting with π - π stacking (ca.3.43 Å) of thiazole ring formed a 2D necklace-like supramolecular chain. These chains formed by N(3)–H(3B)···N(2) and N(3)–H(3A)···N(4) lying paralleled to each other, resulting in a two-dimensional hydrogen-bonded layer along the *ab* and *ac* plane, respectively (Fig. 2). The layers are further extended into a three-dimensional (3D) supramolecular array through hydrogen-bonded interactions, which are offset π - π stacking interactions with the face-to-face distance of ca. 3.43 Å between thiazole rings. Each uncoordinated N3 of thiazole from one chain forms an N···H–O hydrogen bond with a hydroxyl group from another nearby chain. The packing of the title compound can be described as parallel-sandwich geometry (Fig. 2). In addition, 2-aminobenzothiazole (ABT) acts as a donor and 2-((benzothiazol-2-ylimino)methyl)-4,6-di-tert-butylphenol (BYMBP) acts as a acceptor, four ABT occupy the four apical positions, formed the intermolecular hydrogen bond and π - π stacking of the complex when two ABT molecules were antiparallel, simultaneously, each ABT using the amino nitrogen atom and benzothiazole nitrogen atom of BYMBP, forms one kind of hydrogen bonds (N(3)–H(3B)···N(2), Table 1) [20, 21]. Each BYMBP making use of benzothiazole carbon atom and hydroxyl oxygen atom forms the other kind of hydrogen bonds (C(10)–H(10)···O(1), Table 1). Additionally, each ABT making use of thiazole nitrogen atom and amino nitrogen atom forms another kind of hydrogen bonds (N(3)–H(3A)···N(4),

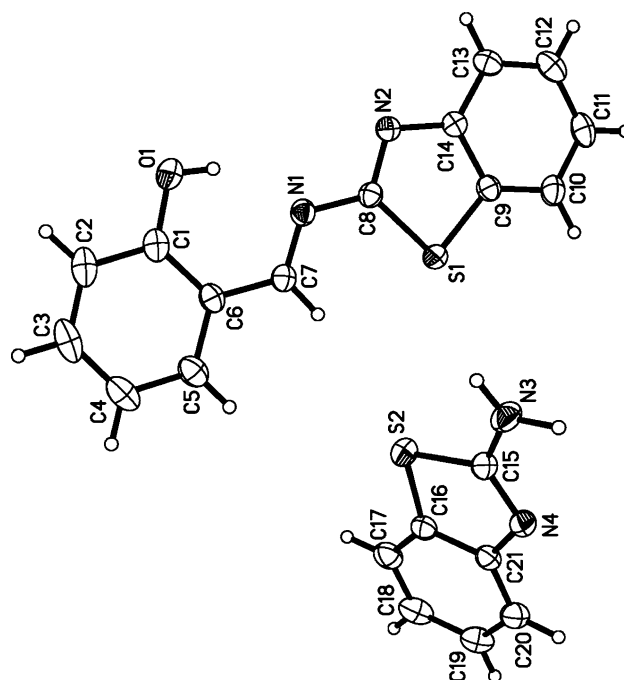
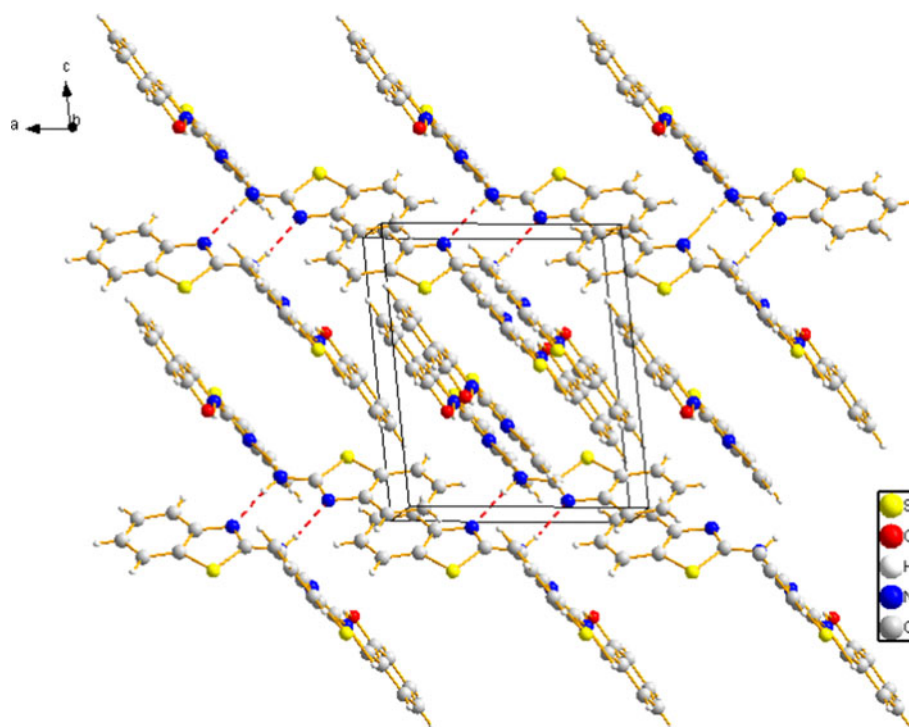
**Fig. 1** Crystal structure of ABT:BYMBP complex

Table 1) in the same formation, and O(1)–H(1)···N(1) are the last hydrogen bonds which are the weakest in this 1:1 complex. It is very interestingly observed in this 2D array, and they are four types of hydrogen-bonded patterns A–D. All calculations were carried out with the RB3LYP/6-311++g(d,p) [18], and the result of the calculations were in accordance with the result of using X-Ray.

RB3LYP/6-311++g(d,p) Calculations

The structures of ABT:BYMBP optimized by the RB3LYP/6-311++g(d,p) [18] approach are shown in Fig. 3. The calculated bond lengths, bond and torsion angles are given in Table 2. Structure (a) shows a monomer of the 1:1 complex in which the hydroxyl group of

Fig. 2 Packing of the ABT:BYMBP complex**Table 1** Selected bond lengths (Å) and angles (°) for ABT:BYMBP complex

Parameters	X-ray	RB3LYP/6-311++g(d,p)	Parameters	X-ray	RB3LYP/6-311++g(d,p)
S(1)–C(9)	1.734(3)	1.757	S(2)–C(16)	1.737(3)	1.764
S(1)–C(8)	1.759(2)	1.820	S(2)–C(15)	1.760(3)	1.792
O(1)–H(1)	0.830	0.995	N(3)–H(3A)	0.898(10)	1.012
N(3)–H(3B)–N(2)	2.122(12)	2.121	N(3)–H(3B)	0.883(10)	1.011
N(3)–H(3A)–N(4)	2.064(11)	2.390	O(1)–H(1)–N(1)	1.87	1.874
C(10)–H(10)–O(1)	2.56	2.555	H(3A)–N(3)–H(3B)	119(3)	114.6
C(16)–S(2)–C(15)	89.27(12)	87.84	C(15)–N(3)–H(3B)	118(2)	113.5
C(9)–S(1)–C(8)	88.66(12)	87.98	C(15)–N(3)–H(3A)	122.2(18)	117.7
C(1)–O(1)–H(1)	109.5	108.0			

All calculations were carried out with the RB3LYP/6-311++g(d,p) level of theory [18]

#1 $-x + 1, -y, -z + 1$; #2 $-x + 1, -y + 1, -z$; #3 $x, y + 1, z$

BYMBP interacts with the amine group of ABT, through the N(3)–H(3B)⋯N(4) hydrogen bond of 2.121 Å, shorter by 0.001 Å than in the crystal (Table 2). In the optimized structure (b) the hydroxyl group of BYMBP is engaged in the N(3)–H(3A)⋯N(4) hydrogen bond, which is by 0.326 Å longer than in the crystal.

X-Ray Crystallography

Diffraction data were collected on a Rigaku Mercury CCD area detector. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were

treated as idealized contributions. The structure was solved and refined using SHELXS-97 programs. Crystal and refinement data for complex are listed in Table 3.

Ultraviolet Spectral Studies

The electronic absorption spectra of the donor (ABT), acceptors (BYMBP) and the resulting complex in ethanol were recorded by UV–vis with a 1 cm quartz cell at room temperature. The ultraviolet spectra of these compounds are shown in Fig. 4. ABT:BYMBP compound shows a moderately intense absorption band at 376 nm, while such a band is absent in the parent ABT. However, at 326 nm for the parent BYMBP, the CT band with a red shift, $\Delta\lambda$

Fig. 3 The optimized structures of ABT:BYMBP by the RB3LYP/6-311++g(d,p) method, **a** monomer connected by the N(3)–H(3B)···N(4) hydrogen bond, **b** monomer connected by N(3)–H(3A)···N(4) hydrogen bond

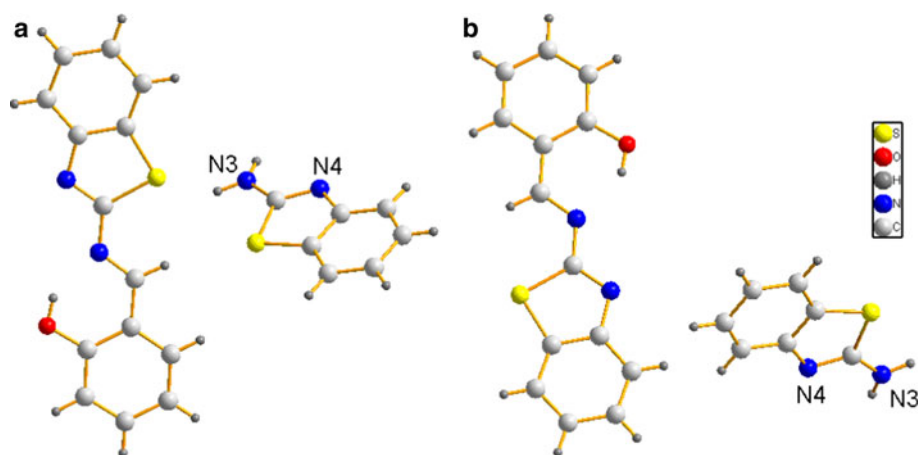


Table 2 Experimental and calculated bond lengths (Å)

Hydrogen bond lengths (Å) and π - π stacking	X-ray	RB3LYP/6-311++g(d,p)
N(3)–H(3A)···N(4)	2.064	2.390
N(3)–H(3B)···N(2)	2.122	2.121
O(1)–H(1)···N(1)	1.87	1.874
C(10)–H(10)···O(1)	2.56	2.555
π - π stacking	3.43 Å	3.43 Å

Table 3 Crystallographic data for complex

Complex	
Formula	C ₂₁ H ₁₆ N ₄ OS ₂
F_w	404.50
T (K)	223(2)
Crystal system	Triclinic
Space group	P-1
a (Å)	9.7732(5)
b (Å)	9.9936(4)
c (Å)	11.0193(7)
β (deg)	78.686(10)
V (Å ³)	958.61(9)
Z	2
D_{calc}	1.401
μ (mm ⁻¹)	0.298
$F(000)$	420
Crystal size (mm)	0.30 × 0.22 × 0.08
θ_{max} (°)	25.50
Reflections collected	8295
Independent reflections	3535
Observed reflections	2724
Parameters refined	263
R	0.0499
wR_2	0.1190
GOF on F^2	1.061

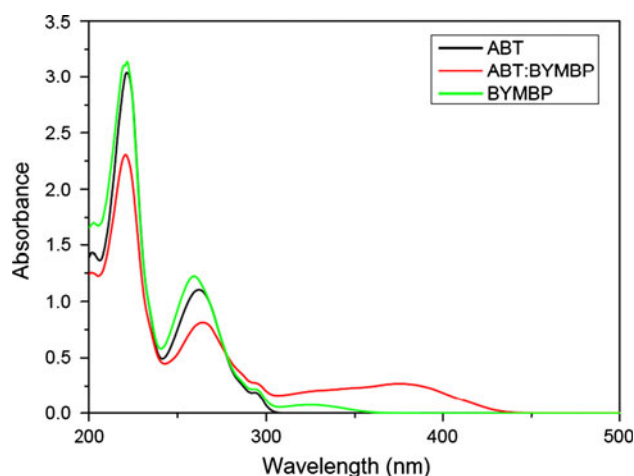


Fig. 4 Absorption spectra of ABT, BYMBP and ABT:BYMBP (10^{-6} mol L⁻¹) in ethanol

about 50 nm, indicates that BYMBP is an efficient electron acceptor, which makes the charge transfer (CT) easier. Thus, ABT:BYMBP compound is a good D-A compound.

Conclusion

The 1:1 complex of BYMBP with ABT was obtained. According to the structure analysis, three chemistry interactions can be seen in its structure, π - π stacking, hydrogen bond and charge transfer. Synthesizing more 1:1 complex remains an important task for further research.

Supplementary Data

Additional crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC reference number is 746489 for the complex. The data can be

obtained free of charge from 178 www.ccdc.cam.ac.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax:+44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk.)

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