



STRUCTURAL
CHEMISTRY

Volume 75 (2019)

Supporting information for article:

Exploring the structural landscape of 2-(thiophen-2-yl)-1,3-benzothiazole: high-*Z* packing polymorphism and cocrystallization with calix[4]tube

Meiry E. Alvarenga, Ana Karoline S. M. Valdo, Leandro Ribeiro, José Antonio Do Nascimento Neto, Debora P. De Araujo, Cleiton Moreira Da Silva, Ângelo De Fátima and Felipe T. Martins

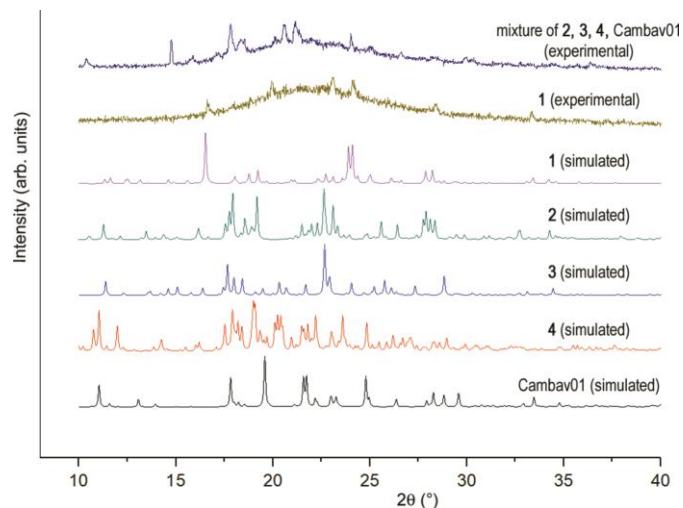


Fig. S1. Simulated powder X-ray diffractograms (PXRD) of 2-(thiophen-2-yl)-1,3-benzothiazole crystal forms and experimental ones of crystallization batches from which crystals of either **1** or **2–4**/Cambav01 (mixture of phases) were isolated out. Analyzes were acquired using a Shimadzu XRD-6000 diffractometer [room temperature (298 K), Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) generated at 40 kV and 30 mA, continuous θ - 2θ scan mode with scan speed $1.000^\circ \text{ min}^{-1}$, acquisition step of 0.020° , divergence and scattering slits at 1.000° , receiving slit at 0.300 mm].

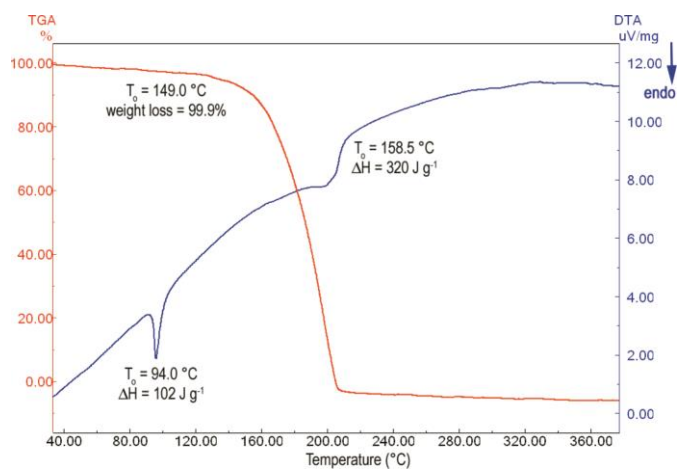


Fig. S2. TG (red line) and DTA (blue line) curves of **1**. Simultaneous thermal analyses were carried out in a Shimadzu DTG-60 thermal analyzer (alumina crucibles, heating rate of 10° min⁻¹ under an N₂ atmosphere at a 50 ml min⁻¹ flow rate).

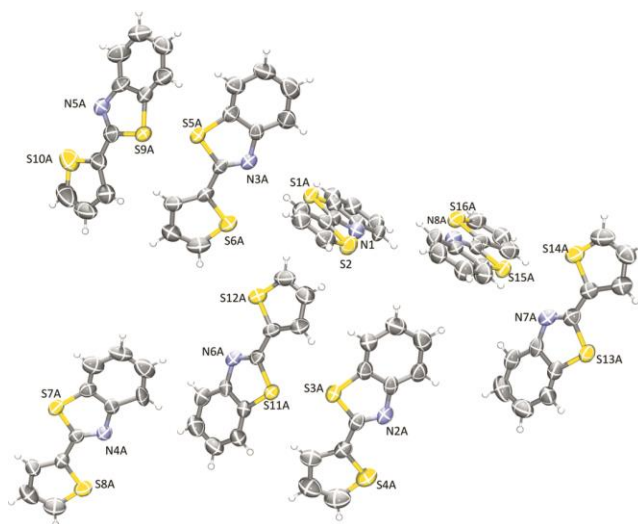


Fig. S3. Asymmetric unit of polymorph **1** (major occupancy part A is shown for all benzothiazole molecules), with label for S and N atoms. Non-H atoms are drawn as ellipsoids at the 50% probability level, while H atoms are represented as white spheres of arbitrary radius.

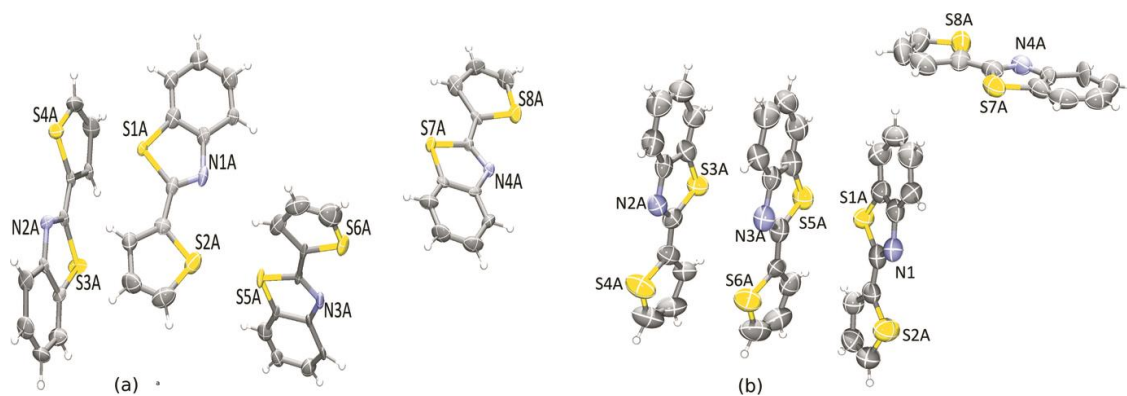


Fig. S4. Asymmetric unit (major occupancy part A is shown for all benzothiazole molecules) in polymorphs (a) **2** and (b) **3**, with labels for S and N atoms. Non-H atoms are drawn as ellipsoids at the 50% probability level, while H atoms are represented as white spheres of arbitrary radius.

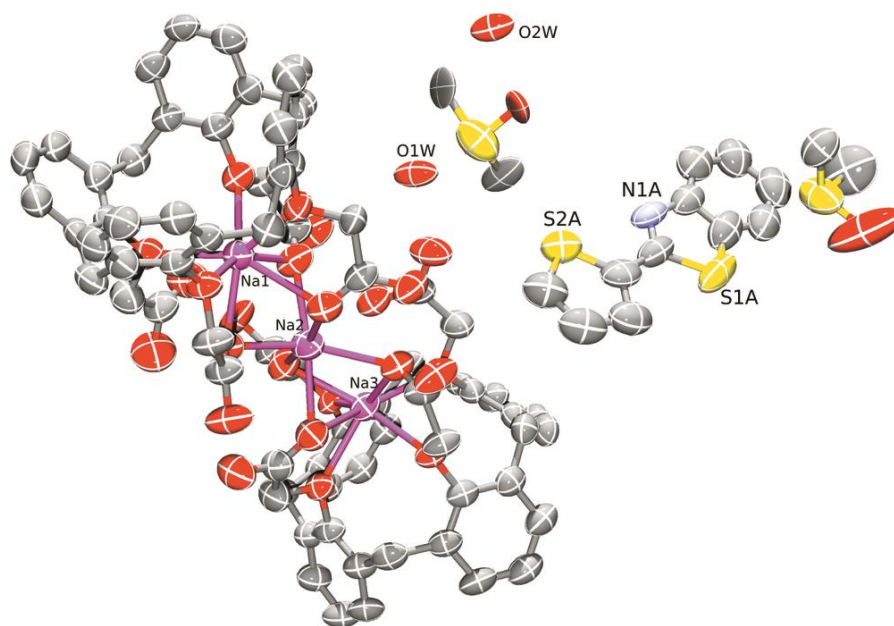


Fig. S5. Asymmetric unit of cocrystal **4** (benzothiazole molecule and the two S atoms from DMSO shown in major occupancy part A). Atom label is shown only for Na atoms, O atoms from water molecules and for S and N atoms from benzothiazole molecule. Non-H atoms are drawn as ellipsoids at the 50% probability level, while H atoms were omitted for clarity.

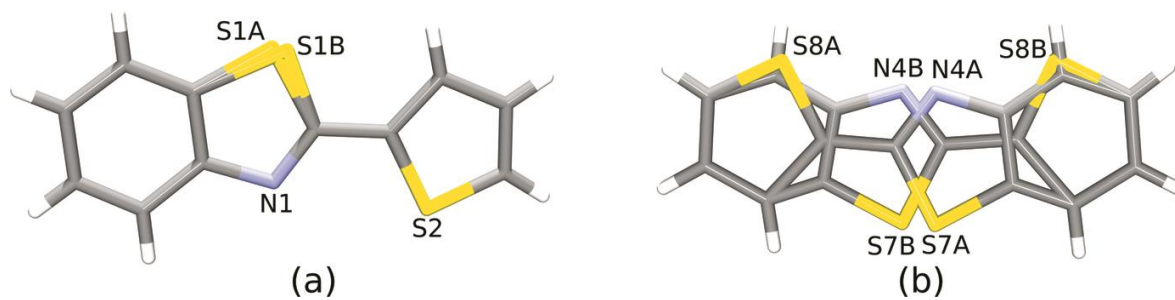


Fig. S6. Examples of disorder of two sites (labelled as A and B) found in benzothiazole molecules in all crystal structures (*a*) only S atom was disordered and (*b*) most atoms disordered, with both parts sharing just six atoms (C atoms from aromatic rings).

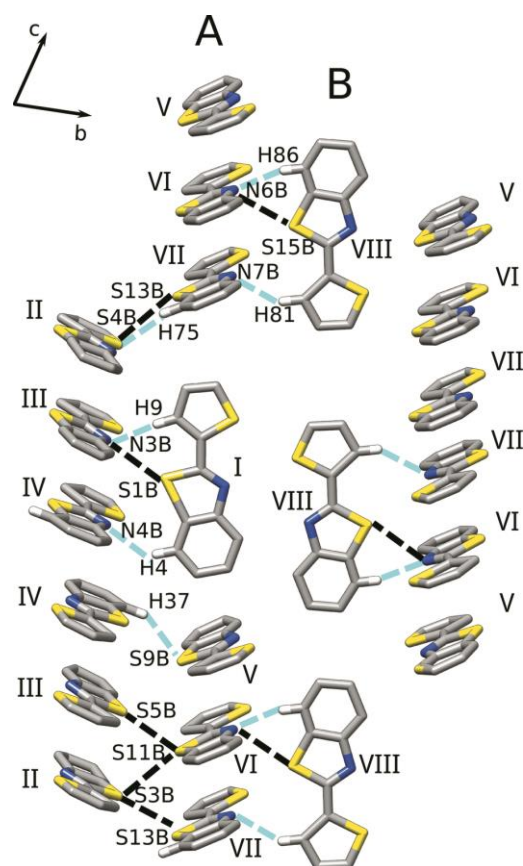


Fig. S7. Intermolecular interactions inside the hexagonal cavity for the minor-occupancy part B is shown for all benzothiazole molecules in polymorph **1**.

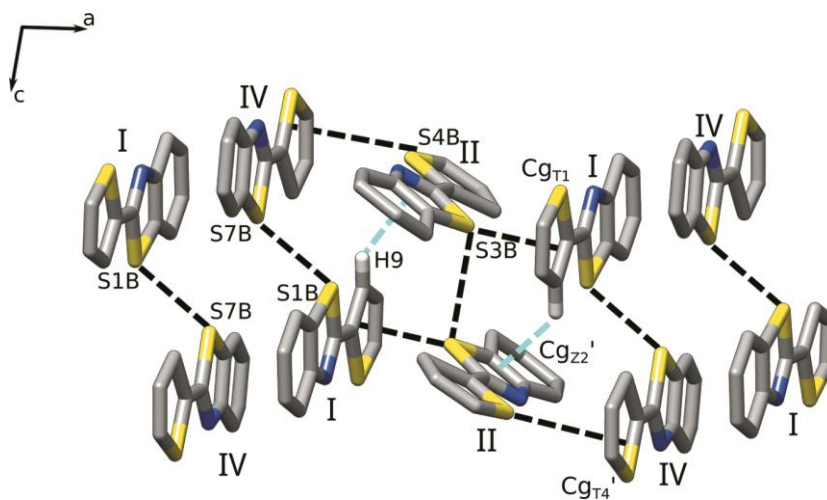


Fig. S8. Intermolecular interactions along the chain for minor occupancy part B is shown for all benzothiazole molecules in polymorph **2**.

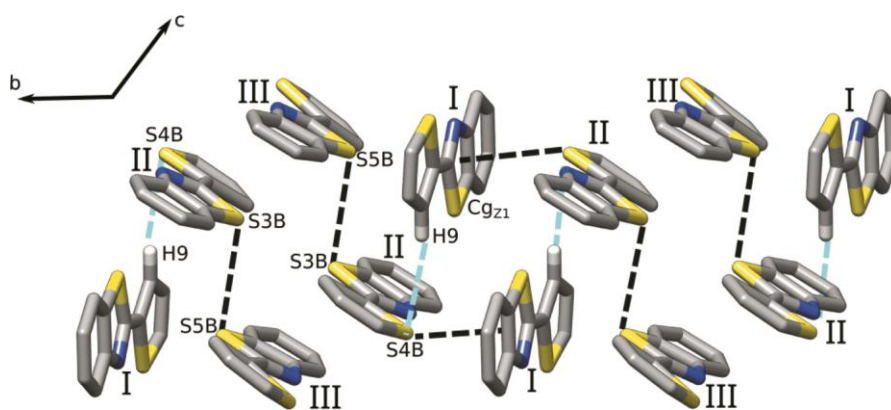


Fig. S9. Intermolecular interactions for minor occupancy part B is shown for all benzothiazole molecules in polymorph **3**, noticing the gain of a C—H...S contact between molecules I and II and again the presence of S...S interactions.

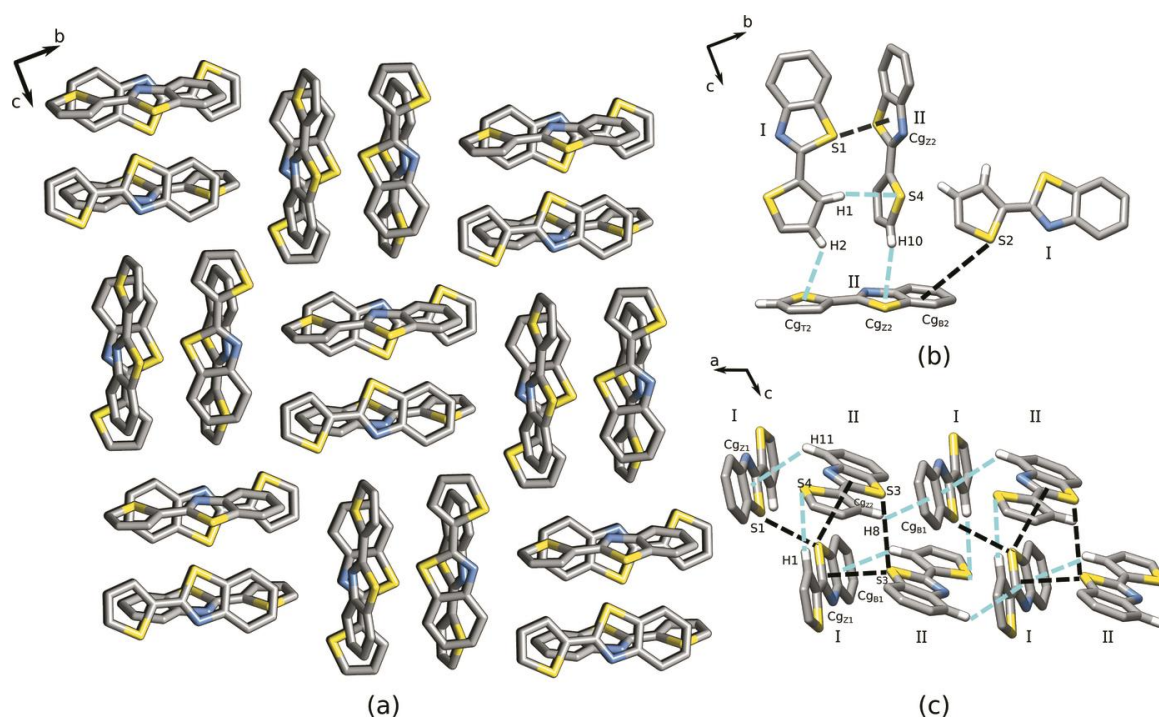


Fig. S10. Packing and interactions found in Cambav01 (Huang *et. al.*, 2016). (a) Whole packing of benzothiazole molecules distributed over to the bc plane. (b) Intermolecular interactions between benzothiazole molecules I and II along the b axis. (c) Chains growing along the a axis showing the alternate disposition of benzothiazole molecules I and II.

STRUCTURAL DESCRIPTION OF DISORDERED PART B AND THE LITERATURE POLYMORPH

All benzothiazole molecules in polymorphs (**1** to **3**) and cocrystal (**4**) exhibited disorder and the refinement led to two sites (A and B), with the minor occupancy part designated as B. The whole packing in all crystal structures didn't change when comparing the major and minor occupancy parts for benzothiazole. Therefore, in polymorphs (**1** to **3**) the formation of hexagonal pattern and the disposition of the chains are maintained, while for cocrystal (**4**) is still observed the alternated layers. Nevertheless, in all polymorphs (**1** to **3**) the presence of S \cdots S interaction is observed strictly when benzothiazole is found in the minor occupancy part B. This contact combined with others altered a few the intermolecular interactions along the triad or inside the hexagonal cavity, as discussed below for each structure.

In minor occupancy part B of polymorph **1**, the main change arose inside the hexagonal cavity (Figure S7). The presence of S \cdots S contacts led to formation of zigzag pattern between molecules III, VI, II and VII. Also, it is noticed the formation of S \cdots π interaction with distance of 4.111(9) Å between S10B and the centroid Cg_{T4'}. Moreover, the distances between centroids of π -stacked rings range from 3.836(2) Å to 4.354(2) Å.

For polymorph **2**, the change is noted along the chain, where most non-classical hydrogen bonds is lost, although $\pi\cdots\pi$, CH $\cdots\pi$, S $\cdots\pi$ interactions are still identified together with the new S \cdots S contacts (Figure S8). The distances between the aromatic ring centroids of molecules I and IV ranges from 3.762(2) to 4.011(2) Å. Meanwhile, the distances between sulfur atom and centroids are 3.387(7) Å (S3B and Cg_{Z1'}) and 3.38(3) Å (S4B and Cg_{Z3'}).

Again, in polymorph **3**, the S $\cdots\pi$ interaction now occurs between sulfur atom S4B from molecule II and centroid Cg_{Z1'}, with a distance between them of 3.793(19) Å. Besides, CH \cdots S pairing and some CH $\cdots\pi$ contacts are lost compared to packing in major occupancy part A, while molecule I is now CH \cdots S interacted with molecule II along the *c* axis (Figure S9). The distance between aromatic rings centroids of π -stacked molecules II and III ranged from 3.922(19) Å to 4.031(19) Å.

Fewer modifications were observed for cocrystal **4** when comparing the disordered parts of benzothiazole molecule, since it does not interact with water and DMSO molecules. Therefore, only interactions between benzothiazole and calix[4]tube were altered. As example, S2B acts now as hydrogen bonding acceptor in two contacts and S1B is not involved in any noteworthy interaction (Table S1).

The crystal structure of 2-(2-thienyl)-1,3-benzothiazole with *Z'* = 2 was already reported by Huang, et. al (Huang *et al.*, 2016). Similarities are found among it and the crystal structures reported here. As seen in Figure S10a, the packing is similar to polymorphs described here, since it features hexagonal cavities. However, the proximity between molecules inside the hexagonal cavity led to absence of hexagonal packing in Cambav01 (Huang *et al.*, 2016). In addition, triads

found in **1** to **3** are not observed in the literature polymorph, as seen in Figure S10b. Otherwise, three molecules interact with each other along *c* axis with completely different geometries found in our crystal structures. Yet, the chains are still observed (Figure S10c), featuring alternated molecules of I and II along the *a* axis. The intermolecular interactions found in Cambav01 (Huang *et al.*, 2016) are also noted in our structures (**1** and **4**), as CH \cdots S, CH \cdots π , S \cdots π and S \cdots S.

Table S1. Hydrogen bond geometry found in structures **1** to **4**, for both disordered parts A and B.

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
1A				
C ₄ -H ₄ ···N _{4A}	0.93	2.69	3.438(10)	138
C ₉ -H ₉ ···N _{3A}	0.93	2.42	3.344(10)	175
C ₁₃ -H ₁₃ ···C _{gB8}	0.93	3.26	3.934(4)	131
C ₂₁ -H ₂₁ ···C _{gB8}	0.93	3.41	4.015(4)	125
C ₂₅ -H ₂₅ ···C _{gZ8}	0.93	3.11	3.827(4)	135
C ₃₁ -H ₃₁ ···S _{11A}	0.93	2.88	3.793(5)	166
C ₃₂ -H ₃₂ ···C _{gZ8}	0.93	3.13	3.796(4)	130
C ₃₆ -H ₃₆ ···C _{gT8}	0.93	2.95	3.771(4)	148
C ₄₃ -H ₄₃ ···C _{gT8}	0.93	3.13	3.769(4)	127
C ₄₇ -H ₄₇ ···C _{gB1}	0.93	3.00	3.854(3)	154
C ₅₄ -H ₅₄ ···C _{gB1}	0.93	3.20	3.805(5)	125
C ₅₈ -H ₅₈ ···C _{gZ1}	0.93	3.47	4.115(4)	128
C ₆₆ -H ₆₆ ···S _{1A}	0.93	2.99	3.872(4)	158
C ₆₉ -H ₆₉ ···C _{gT1}	0.93	3.36	3.955(4)	124
C ₇₇ -H ₇₇ ···C _{gT1}	0.93	3.20	3.897(5)	133
C ₈₁ -H ₈₁ ···N _{7A}	0.93	2.71	3.519(16)	146
C ₈₆ -H ₈₆ ···N _{6A}	0.93	2.52	3.424(12)	163
1B				
C ₂ -H ₂ ···S _{10B}	0.93	2.99	3.771(8)	143
C ₄ -H ₄ ···N _{4B}	0.93	2.60	3.35(2)	138

C ₉ -H ₉ •••N _{3B}	0.93	2.37	3.30(3)	172
C ₁₃ -H ₁₃ •••C _{gT8} '	0.93	3.23	3.882(5)	129
C ₂₁ -H ₂₁ •••C _{gT8} '	0.93	3.31	3.954(4)	128
C ₂₄ -H ₂₄ •••C _{gZ8} '	0.93	3.30	3.969(4)	130
C ₃₃ -H ₃₃ •••C _{gZ8} '	0.93	3.13	3.811(5)	132
C _{37B} -H _{37B} •••S _{9B}	0.93	2.74	3.55(4)	147
C ₃₆ -H ₃₆ •••C _{gB8} '	0.93	3.01	3.830(4)	148
C ₄₃ -H ₄₃ •••C _{gB8} '	0.93	3.16	3.785(4)	127
C ₄₇ -H ₄₇ •••C _{gB1} '	0.93	3.00	3.854(3)	154
C ₅₄ -H ₅₄ •••C _{gB1} '	0.93	3.20	3.805(5)	125
C ₅₇ -H ₅₇ •••C _{gZ1} '	0.93	3.42	4.059(4)	128
C ₆₆ -H ₆₆ •••S _{1B}	0.93	3.03	3.89(2)	154
C ₆₈ -H ₆₈ •••C _{gT1} '	0.93	3.29	3.893(4)	125
C ₇₅ -H ₇₅ •••S _{4B}	0.93	2.93	3.81(2)	159
C ₇₇ -H ₇₇ •••C _{gT1} '	0.93	3.20	3.897(5)	133
C ₈₁ -H ₈₁ •••N _{7B}	0.93	2.57	3.38(2)	147
C ₈₆ -H ₈₆ •••N _{6B}	0.93	2.40	3.30(4)	165

2A

C ₂ -H ₂ •••C _{gB3}	0.93	3.59	4.213(6)	127
C _{12A} -H _{12A} •••C _{gB4}	0.93	2.86	3.58(3)	134
C ₁₃ -H ₁₃ •••C _{gB3}	0.93	3.04	3.819(5)	143
C ₁₅ -H ₁₅ •••C _{gB1}	0.93	2.98	3.692(7)	134
C _{20A} -H _{20A} •••C _{gT1}	0.93	2.94	3.759(6)	147

C ₂₁ -H ₂₁ •••C _{gB3}	0.93	2.82	3.605(5)	143
C ₂₂ -H ₂₂ •••C _{gZ3}	0.93	3.36	4.144(6)	143
C ₂₅ -H ₂₅ •••N _{4A}	0.93	2.68	3.37(19)	132
C ₃₁ -H ₃₁ •••N _{1A}	0.93	2.64	3.423(7)	142
C ₃₆ -H ₃₆ •••C _{gZ3}	0.93	3.18	3.937(5)	139
C ₄₂ -H ₄₂ •••S _{7A}	0.93	2.95	3.853(7)	164
C ₄₃ -H ₄₃ •••C _{gT3}	0.93	3.24	4.037(5)	145

2B

C ₃ -H ₃ •••C _{gB3} '	0.93	3.53	4.222(6)	133
C ₉ -H ₉ •••C _{gZ2} '	0.93	3.17	3.915(6)	139
C _{12B} -H _{12B} •••C _{gB4} '	0.93	2.97	3.69(4)	135
C ₁₃ -H ₁₃ •••C _{gT3} '	0.93	3.04	3.788(5)	138
C ₁₅ -H ₁₅ •••C _{gT1} '	0.93	3.02	3.730(5)	134
C _{20B} -H _{20B} •••C _{gB1} '	0.93	3.32	3.80(3)	114
C ₂₁ -H ₂₁ •••C _{gT3} '	0.93	2.79	3.612(5)	148
C ₂₅ -H ₂₅ •••N _{4B}	0.93	2.67	3.38(19)	134
C ₂₆ -H ₂₆ •••N _{2B}	0.93	2.72	3.47(2)	138
C ₃₁ -H ₃₁ •••N _{1B}	0.93	2.58	3.36(3)	142
C ₃₆ -H ₃₆ •••C _{gZ3} '	0.93	2.97	3.719(5)	138
C ₄₃ -H ₄₃ •••C _{gZ3} '	0.93	3.11	3.918(5)	146
C ₄₄ -H ₄₄ •••S _{2B}	0.93	3.08	3.68(2)	124

3A

C _{1A} -H _{1A} •••C _{gB3}	0.93	2.96	3.561(6)	123
C ₃ -H ₃ •••C _{gT4}	0.93	2.97	3.795(4)	149
C ₄ -H ₄ •••C _{gT2}	0.93	3.11	3.809(8)	134
C ₉ -H ₉ •••C _{gB2}	0.93	2.83	3.574(6)	138
C ₁₀ -H ₁₀ •••C _{gT4}	0.93	3.13	3.802(4)	132
C ₁₄ -H ₁₄ •••C _{gZ4}	0.93	3.00	3.838(4)	151
C ₂₀ -H ₂₀ •••S _{3A}	0.93	2.96	3.868(8)	166
C ₂₁ -H ₂₁ •••C _{gZ4}	0.93	3.12	3.782(5)	129
C ₂₄ -H ₂₄ •••C _{gB4}	0.93	3.41	4.044(5)	127
C ₃₃ -H ₃₃ •••C _{gB4}	0.93	3.51	4.258(6)	139
C ₃₇ -H ₃₇ •••N _{3A}	0.93	2.59	3.481(14)	160

3B

C ₃ -H ₃ •••C _{gB4} '	0.93	2.96	3.804(4)	152
C ₉ -H ₉ •••S _{4B}	0.93	2.98	3.878(17)	162
C ₁₀ -H ₁₀ •••C _{gB4} '	0.93	3.09	3.809(4)	135
C ₁₄ -H ₁₄ •••C _{gZ4} '	0.93	3.18	4.002(4)	148
C ₂₂ -H ₂₂ •••C _{gZ4} '	0.93	3.86	4.395(6)	120
C ₂₄ -H ₂₄ •••C _{gT4} '	0.93	3.36	3.995(5)	128
C ₃₃ -H ₃₃ •••C _{gT4} '	0.93	3.40	4.167(6)	141
C ₃₆ -H ₃₆ •••N _{2B}	0.93	2.74	3.554(19)	146
C ₃₇ -H ₃₇ •••N _{3B}	0.93	2.48	3.37(3)	160

4

C ₃₇ -H _{37B} •••O _{1W}	0.97	2.44	3.385(14)	163
--	------	------	-----------	-----

C ₅₅ -H _{55A} •••O _{1S}	0.97	2.53	3.370(16)	144
C ₆₈ -H ₆₈ •••C _{g2}	0.93	3.29	4.060(10)	142
C ₆₉ -H ₆₉ •••C _{g3}	0.93	2.98	3.800(10)	148
O ₃ -H _{3C} •••O _{2W}	0.82	1.89	2.558(15)	137
O ₉ -H _{9C} •••O ₂₄	0.82	1.62	2.420(11)	165
O ₁₂ -H _{12C} •••O ₂₀	0.82	1.68	2.483(9)	165
O ₁₅ -H _{15C} •••O ₆	0.82	1.68	2.490(10)	168
O ₁₈ -H _{18C} •••O ₂	0.82	1.83	2.633(9)	168
O _{1W} -H _{1wA} •••O _{2S}	1.00	1.94	2.722(15)	132
O _{1W} -H _{1wB} •••O ₂₁	1.00	1.88	2.755(13)	144
O _{2W} -H _{2wA} •••O _{1S}	1.00	1.64	2.646(19)	177
O _{2W} -H _{2wB} •••O ₆	0.98	2.15	2.736(12)	116
O _{2W} -H _{2wB} •••O ₁₅	0.98	2.46	3.248(12)	136

4A

C ₄₆ -H _{46B} •••S _{1A}	0.97	2.92	3.453(18)	116
C ₄₈ -H _{48A} •••N _{1A}	0.97	2.62	3.52(2)	154
C ₅₂ -H ₅₂ •••C _{gT1}	0.93	3.18	3.950(11)	142
C ₆₀ -H ₆₀ •••C _{gB1}	0.93	2.84	3.727(11)	160
C ₇₉ -H ₇₉ •••S _{2A}	0.93	2.95	3.78(2)	149
C _{4S} -H _{4S1} •••C _{g4}	0.96	2.81	3.732(11)	161
C _{4S} -H _{4S2} •••C _{g6}	0.96	2.87	3.389(10)	115
C _{4S} -H _{4S3} •••C _{g5}	0.96	3.01	3.683(13)	128

4B				
C ₂₁ -H _{21A} ····S _{2B}	0.97	2.93	3.58(2)	125
C ₄₈ -H _{48A} ····N _{1B}	0.97	2.62	3.562(19)	164
C ₅₂ -H ₅₂ ····C _{Z1'}	0.93	3.05	3.90(19)	152
C ₆₀ -H ₆₀ ····S _{2B}	0.93	2.83	3.68(2)	153
C _{4S} -H _{4S4} ····C _{g5}	0.96	2.83	3.683(13)	149
C _{4S} -H _{4S5} ····C _{g7} *	0.96	2.29	3.525(9)	120
C _{4S} -H _{4S6} ····C _{g6}	0.96	2.53	3.389(10)	149

* C_{g7} was calculated through the atoms C49-C54 from benzene ring from calix[4]tube of cocrystal.

Table S2. Distance between centroid and sulfur atom (S···π) or centroid...centroid range found in polymorphs **1** to **3** for benzothiazole molecules in major occupancy part A.

Polymorph	π···π (Å)	S···π(Å)
1	3.852(2) – 4.057(2)	3.451(6)
2	3.738(2) – 4.122(2)	3.464(19) and 3.587(3)
3	3.872(19) – 4.035(19)	3.664(3) and 3.642(3)

Table S3. Intermolecular interactions of benzothiazole molecules with each other (**1 to 3**) and with calix[4]tube (**4**) for both disordered parts A and B.

1		2		3		4
A	B	A	B	A	B	A and B
CH···N	CH···N	CH···N	CH···N	CH···N	CH···N	CH···N
CH···S	CH···S	CH···S	CH···π	CH···S	CH···S	CH···S
CH···π	S···π	CH···π	S···π	CH···π	CH···π	CH···π
S···N	S···N	S···π	S···S	S···π	S···π	
	S···S				S···S	