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The first observation of *cis* and *trans* isomers for bibenzo[*d*]imidazole-based compounds influenced by halogen substituent effects

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ABSTRACT

A pair of bibenzo[*d*]imidazole-based *cis–trans* positional isomers have been obtained *via* the condensation between biphenyl-3,3′,4,4′-tetraamine and 3,5-dichloro-2-hydroxybenzaldehyde, and they can be isolated by the following spontaneous crystallization in *N*,*N*-dimethylformamide (DMF) and manual separation. Halogen substituent effects are believed to be responsible for the successful isolation of *cis* and *trans* isomers, which could be further supported by density function theory (DFT) calculations. To our knowledge, this is the first structural report on the *cis–trans* isomerism for this family of compounds.

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Recently, bibenzo[*d*]imidazole derivatives [1] are significant heterocyclic compounds and they are particularly useful as biologically active compounds and intermediates in pharmaceutical chemistry [2]. As we know, there is *cis–trans* constitutional isomerism in this family of compounds because the two protons of imidazole rings (NH) can point toward the same (*cis*) or the opposite (*trans*) direction of molecular plane. Unlike the traditional *cis–trans* isomerism in the double-bond system, free rotation of the central single bond between the two benzo[*d*]imidazole units can be restricted also generating the *cis–trans* tautomerism, because of the large steric hindrance effects of the attached groups on both sides. Constigurational isomerism [3–6], as one of the geometrical isomerisms, is not only important to the fine chemical manufacturers but also to other areas of chemistry. Tautomers in distinctive isomeric forms have different properties such as pharmacological effects, crystal habits, helicity and chirality in the solid state and in the bulk [7–10]. Single-crystal X-ray diffraction method is proved to be the most powerful tool to characterize various geometrical isomerisms by its measured bond lengths and angles, dihedral and torsion angles, *etc.* The subtle alteration of functional groups, the different tautomeric forms and crystallographic arrangements help to decide their properties.

In this paper, an isomeric pair of bibenzo[*d*]imidazole-based compounds (*cis* and *trans* positional isomers of **BBI-4Cl**), together with a *cis* isomer of **BBI-4Br**, have been obtained *via* the classical condensation [11] between biphenyl-3,3′,4,4′-tetraamine and 3,5-dichloro-2-hydroxybenzaldehyde (or 3,5-dibromo-2-hydroxybenzaldehyde) and the following spontaneous crystallization [12–14] in DMF and mechanical separation. Halogen substituent effects, intramolecular O–H···N hydrogen bonds and molecular planarity are believed to help the successful formation of *cis* and *trans* isomers of **BBI-4Cl** simultaneously [15]. Distinguishable single-crystal growing habits of them make possible the separation and structural characterization. DFT calculations have been done to further compare the differences between the molecular conformations and spectral properties of these *cis* and *trans* isomers. To the best of our knowledge, this is the first structural report on *cis–trans* isomerism for this family of compounds.

Compounds **BBI-4Cl** and **BBI-4Br**, having the same bibenzo[*d*]imidazole/phenol skeleton shown in Scheme 1, were prepared in satisfactory yields (62 and 56%) [16]. It is worthwhile to note that this synthetic method has the advantages of easy to operate, easy work-up and few by-products. When DMF was used as the reaction solvent and 4 Å molecular sieves were added as the catalyst in the synthetic process, the yields have been slightly increased. The proposed formation mechanism [11,17] for compounds **BBI-4Cl** and **BBI-4Br** was given in Scheme SI1. At first, the condensation between biphenyl-3,3′,4,4′-tetraamine and halogenated salicylaldehyde afforded the bis-Schiff base **1**, and then the intramolecular nucleophilic addition reaction took place to produce bis-imidazolidine **2**. Finally, the bisimidazole compound was obtained by the oxidative cyclodehydrogenation of intermediate **2**.

UV–Vis absorption and fluorescence emission spectra of compounds **BBI-4Cl** and **BBI-4Br** in their methanol solutions with the same concentration of 1.0×10^{-4} mol/L were recorded at room temperature, respectively, in order to compare the differences originated from their molecular structures. Similar optical properties have been shown in this case, which agree well with the following theoretical results. As illustrated in Fig. 1, due to the presence of large delocalized π-system, strong absorption bands at 359 ($\varepsilon = 64600$) and 361 ($\varepsilon = 70900$) nm are assigned to the π–π^* transition between the bibenzo[*d*]imidazole rings and the phenol units in compounds **BBI-4Cl** and **BBI-4Br**, which are analogous to the previously reported aromatic bis(*o*-aminoanils) compounds (340–360 nm) [11,17]. The fluorescence spectra of compounds **BBI-4Cl** and **BBI-4Br** at room temperature illustrate a large

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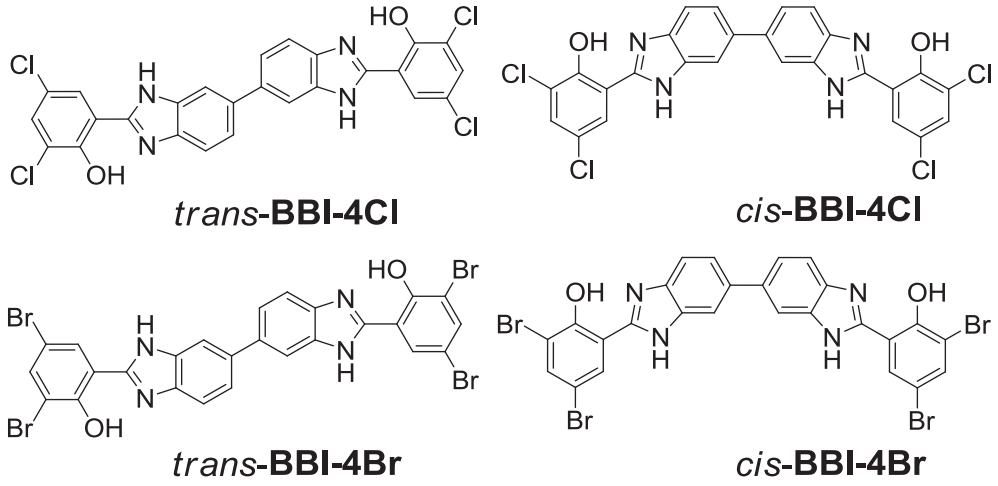

Scheme 1. Molecular structures of different *cis* and *trans* isomers for **BBI-4Cl** and **BBI-4Br** having the same bibenzo[*d*]imidazole/phenol skeleton.

Stokes shift, where strong green emission peaks at 476 and 478 nm are found for **BBI-4Cl** and **BBI-4Br**, respectively, upon the same excitation at 290 nm. A small bathochromic shift of 2 nm from **BBI-4Cl** to **BBI-4Br** is suggested to originate from the halogenated effects in their molecular structures.

The dark-yellow single crystals of *trans*-**BBI-4Cl**·$(DMF)_2$, *cis*-**BBI-4Cl**·$(DMF)_2$ and *cis*-**BBI-4Br**·$(DMF)_2$ suitable for X-ray diffraction measurement were grown from DMF by slow evaporation in air at room temperature for 2–3 weeks [18]. It is very interesting to point out that the spontaneous formation of single crystals for the *cis* and *trans* positional isomers of **BBI-4Cl** can be attained in DMF. The yellow crystals of two structural isomers have different shapes and growing habits. Namely, the needle crystals of *trans*-**BBI-4Cl**·$(DMF)_2$ grow radially as a single colony from the first-appearing nucleus, while the block crystals of *cis*-**BBI-4Cl**·$(DMF)_2$ grow separately at the bottom of the beaker. So they can be collected individually by careful manual separation and used for X-ray single-crystal diffraction measurement successfully. In contrast, the same experimental protocol has been used to prepare the *cis* and *trans* isomers of **BBI-4Br**, where the four chlorine atoms of two side phenol rings are replaced by bromine atoms. As a result, only *cis*-**BBI-4Br**·$(DMF)_2$ is obtained and further verified by X-ray single-crystal diffraction determination. However, the attempt to obtain the *trans* isomer of **BBI-4Br** has not been successful. The phase purity of three compounds in this work has been further confirmed by the PXRD patterns (Fig. SI2 in Supporting information), in which the simulated patterns generated from the results of single-crystal diffraction data and as-synthesized ones are almost identical, demonstrating good phase purity of the products.

X-ray structural analyses of three compounds *trans*-**BBI-4Cl**·$(DMF)_2$, *cis*-**BBI-4Cl**·$(DMF)_2$ and *cis*-**BBI-4Br**·$(DMF)_2$ reveal that the *cis* and *trans* isomers have obviously different unit cells and *cis*-**BBI-4Cl**·$(DMF)_2$ and *cis*-**BBI-4Br**·$(DMF)_2$ are isomorphous structures. As can be seen in Fig. 2, the two protons of imidazole rings point toward the opposite direction of molecular plane of *trans*-**BBI-4Cl**·$(DMF)_2$, while they point to same direction of molecular planes in the cases of *cis*-**BBI-4Cl**·$(DMF)_2$ and *cis*-**BBI-4Br**·$(DMF)_2$. The middle two benzoimidazole rings of three compounds are essentially coplanar with the dihedral angles of zero for *trans*-**BBI-4Cl**·$(DMF)_2$ and 4.3(5) and 1.2(8)° for *cis*-**BBI-4Cl**·$(DMF)_2$ and *cis*-**BBI-4Br**·$(DMF)_2$. It is worthwhile to mention that strong intramolecular O–H···N hydrogen bonding interactions (Table SI2) are found with the H···A distances of 1.82(1) Å in *trans*-**BBI-4Cl**·$(DMF)_2$, 1.80(1) and 1.81(1) Å in *cis*-**BBI-**

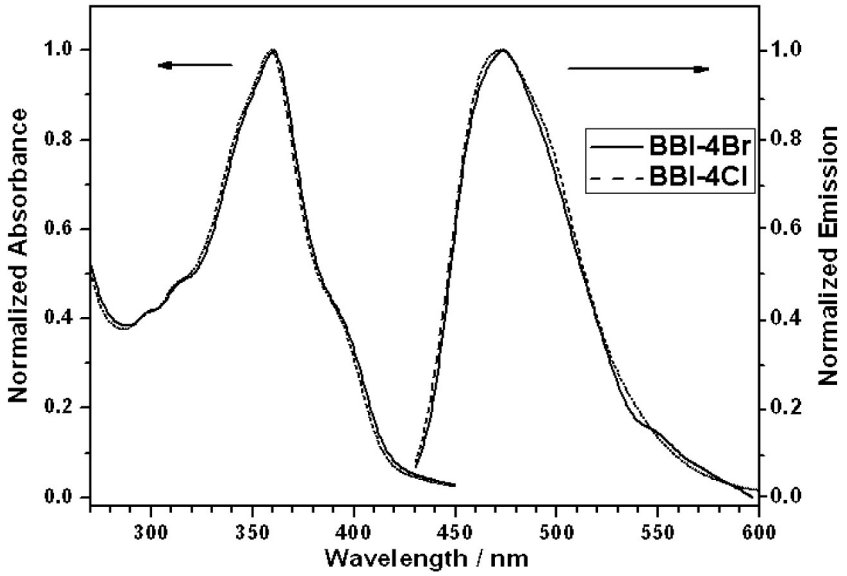

Fig. 1. UV–Vis absorption (left) and fluorescence emission (right) spectra of compounds **BBI-4Cl** and **BBI-4Br** recorded in their methanol solutions with the same concentration of 1.0×10^{-4} mol/L.

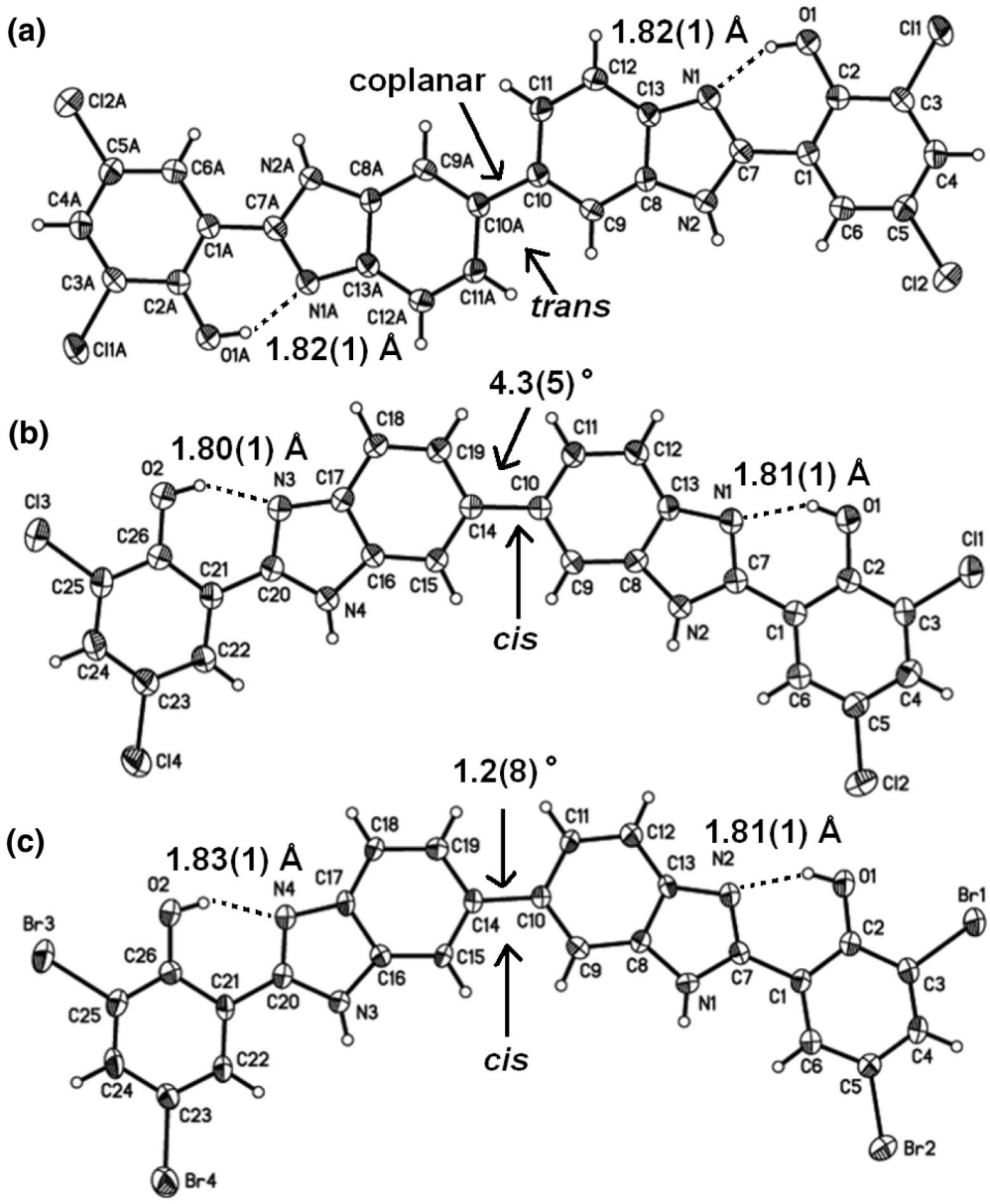

Fig. 2. ORTEP drawings of *trans*-**BBI-4Cl**·$(DMF)_2$ (a), *cis*-**BBI-4Cl**·$(DMF)_2$ (b) and *cis*-**BBI-4Br**·$(DMF)_2$ (c) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Solvent molecules are omitted for clarity.

4Cl·$(DMF)_2$, 1.81(1) and 1.83(1) Å in *cis*-**BBI-4Br**·$(DMF)_2$. As a result, six-membered C_3NOH hydrogen-bonding rings are formed, which should be helpful to fix the configuration between the substitutional phenol and imidazole skeleton. Because of the steric hindrance effects of two fused four-ring units on both sides, the free rotation of the middle C – C single bond (1.49(1) Å in length, Table SI1) is blocked to some extent and the presence of different *cis* and *trans* positional isomers is possible in the solid state.

As can be shown in Fig. 3, similar crystal packing modes are found for three compounds *trans*-**BBI-4Cl**·$(DMF)_2$, *cis*-**BBI-4Cl**·$(DMF)_2$ and *cis*-**BBI-4Br**·$(DMF)_2$, where contiguous molecules are linked by different intermolecular hydrogen-bonding and π–π stacking interactions into two-dimensional supramolecular networks.

On the one hand, distinguishable results on the structures of *cis* and *trans* isomers of **BBI-4Cl** and **BBI-4Br** prompt us to seek further theoretic supports on the halogen substituent effects since the only structural difference is the replacement of four chlorine atoms with four bromine atoms at the same positions of two side phenol rings. On the other hand, single-crystal diffraction data for a pair of *cis* and *trans* positional isomers generally are good candidates for density function theory (DFT) computational studies on comparing the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gaps and energy barriers of different isomers with their spectral data.

Based upon the above-mentioned considerations, DFT computational studies are carried out to make contrastive studies, where the fixed atom coordinates of four compounds are used for the isomeric energy barrier and HOMO–LUMO gap calculations. All calculations are carried out with Gaussian03 programs [19] by B3LYP method and 6-31G* basis set without any symmetry constraints. The computational results given in Table 1 reveal that the resultant HOMO–LUMO gaps for *cis* and *trans* isomers of **BBI-4Cl** and **BBI-4Br** are 3.66, 3.61, 3.65 and 3.60 eV, which are in agreement with their UV–Vis absorptions. As depicted in Fig. 4, subtle changes are observed in the calculated spatial representations of HOMOs and LUMOs because of the influences of introducing different halogen groups (four Cl *versus* four Br) in the two side phenol rings. The middle C – C single bond length is also similar to the single-crystal data, and the dihedral angles between the benzoimidazole and the phenol units and those between the

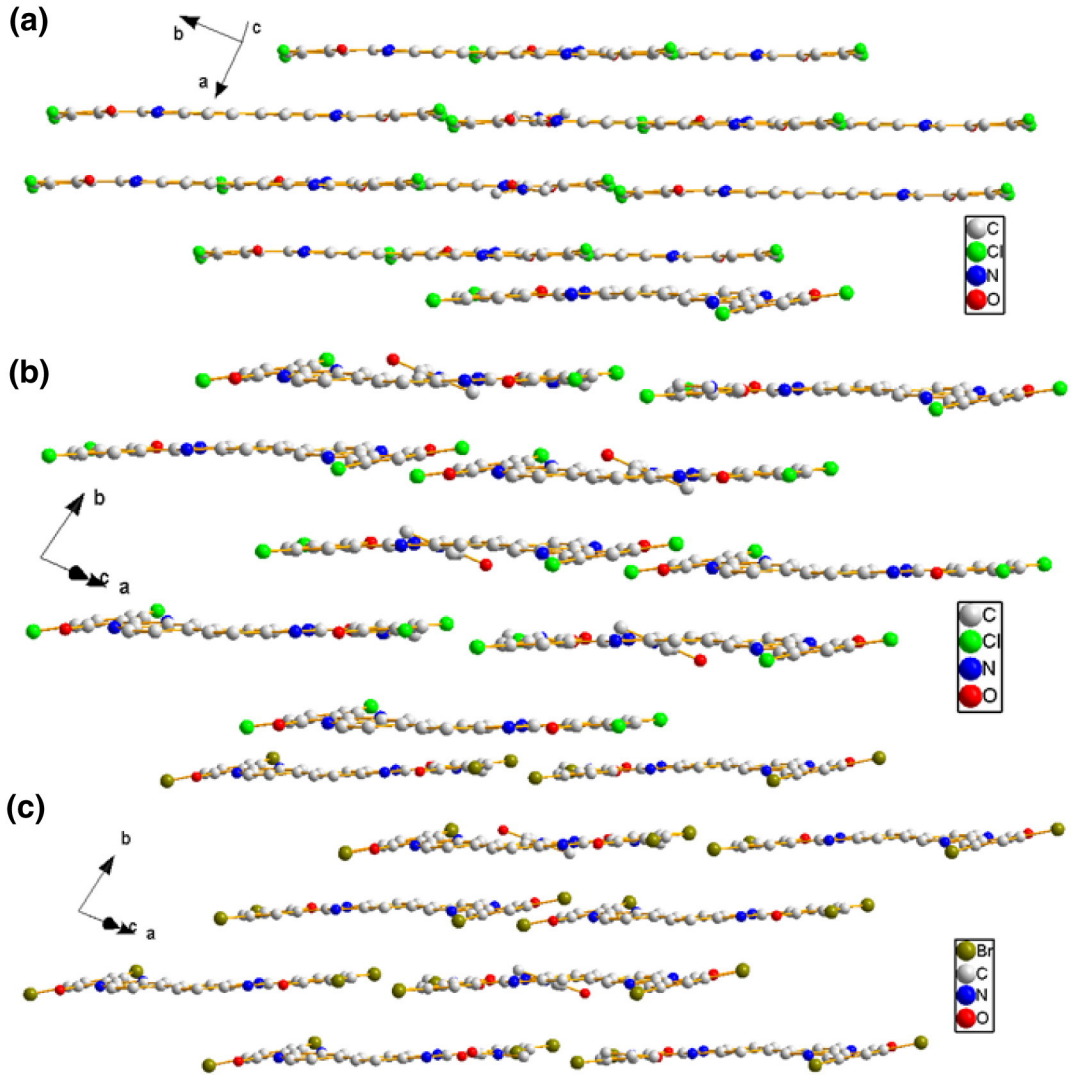

Fig. 3. Perspective view and schematic illustration of the packing structures of compounds *trans*-**BBI-4Cl**·$(DMF)_2$ (a), *cis*-**BBI-4Cl**·$(DMF)_2$ (b) and *cis*-**BBI-4Br**·$(DMF)_2$ (c).

benzoimidazole rings are very close to zero showing excellent planarity of the whole molecules. Nevertheless, it is noted that the energy barrier for *cis* and *trans* isomers (isomerization energy $\Delta E_{cis-trans}$) of **BBI-4Cl** and **BBI-4Br** is significantly different (4.95 *versus* 1.75 kJ/mol), since different halogen with different heavy atom effects can impact the energy barrier between the constigurational isomerism. As we know, too large or too small isomerization energy tends to form only one type of stable isomer, but suitable isomerization energy will make possible the successful isolation of *cis* and *trans* isomers individually in the process of crystallization. So in our case, **BBI-4Cl** has more suitable isomerization energy for the isolation of *cis* and *trans* isomers individually in comparison with **BBI-4Br**, which can be verified by our experimental results. Furthermore, DMF molecules are believed to play an important role in the kinetic control of the solvent-induced crystallization.

Table 1
Calculated HOMO–LUMO gaps and energy barriers for *cis* and *trans* isomers of **BBI-4Cl** and **BBI-4Br** for comparisons.

Compound	$Eg^{opt[a]}$ (eV)	$Eg^{calcd[b]}$ (eV)	$\Delta E^{[c]}$ (kJ/mol)	$d^{[d]}_{C-C}$ (Å)
cis-**BBI-4Cl**	3.45	3.62	4.95	1.493
trans-**BBI-4Cl**		3.66		
cis-**BBI-4Br**	3.43	3.61	1.75	1.485
trans-**BBI-4Br**		3.65		

[a]Optical gap from normalized absorption spectra.
[b]HOMO–LUMO gap calculated by DFT B3LYP/6-31G* level.
[c]Energy barrier for *cis* and *trans* isomers.
[d]Mean middle C–C single bond length after full optimization.

In summary, this is a study on the supramolecular *cis–trans* isomerization and spontaneous crystallization in the solid state. We have described herein the single-crystal structures of a pair of *cis–trans* isomers of bibenzo[*d*]imidazole-based compounds *trans*-**BBI-4Cl**·$(DMF)_2$ and *cis*-**BBI-4Cl**·$(DMF)_2$ together with a *cis* isomer of **BBI-4Br**·$(DMF)_2$. They are prepared *via* the condensation between biphenyl-3,3′,4,4′-tetraamine and 3,5-dichloro-2-hydroxybenzaldehyde (or 3,5-dibromo-2-hydroxybenzaldehyde), and they can be isolated by the following spontaneous crystallization in DMF and manual separation. Halogen substituent effects, intramolecular O–H···N hydrogen bonds and molecular planarity are believed to be responsible for the successful formation of *cis* and *trans* isomers of **BBI-4Cl**. Distinguishable growing habits of *cis* and *trans* single crystals of **BBI-4Cl** make possible the separation and structural characterization of them.

Specifically, the real issue here is the interconversion between the *cis* and *trans* isomers in the solution state. The fact that the *cis* and *trans* crystals are observed for **BBI-4Cl** would mean that both the *cis* and *trans* configurations are present in significant proportions in solution. As for **BBI-4Br**, it seems that the *cis* isomer is dominant in solution. DFT calculations have been done to give a theoretic support on the possible isolation of *cis* and *trans* positional isomers individually, where a

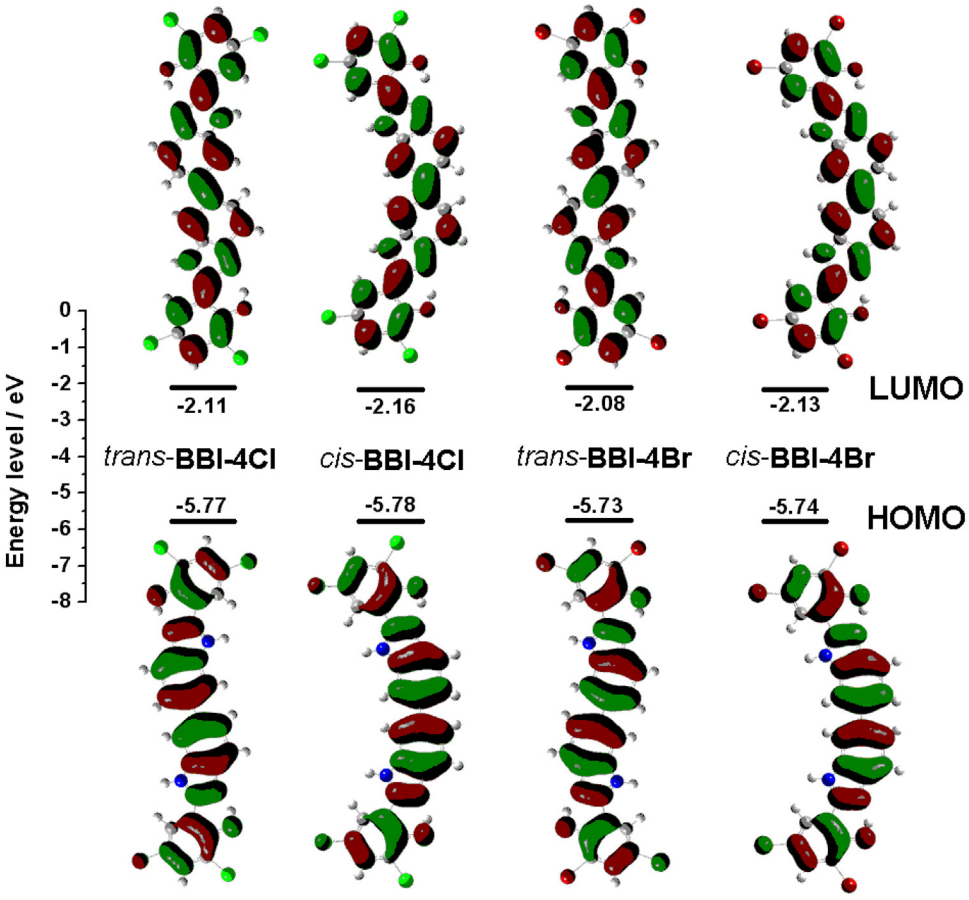

Fig. 4. The HOMO and LUMO energy levels and their molecular orbital distributions of compounds *trans*-**BBI-4Cl**, *cis*-**BBI-4Cl**, *trans*-**BBI-4Br** and *cis*-**BBI-4Br**.

more suitable $\Delta E_{cis-trans}$ value for **BBI-4Cl** is found. So, it is suggested that the *cis* and *trans* isomers of **BBI-4Br** convert to each other more easily than **BBI-4Cl**, and this assumption can explain our experimental and computational result. To the best of our knowledge, this is the first structural report on the *cis–trans* structural isomers and a special case of spontaneous crystallization in the bibenzo[*d*]imidazole system.

Acknowledgments

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Appendix A. Supplementary material

CCDC reference numbers 896866–896868 for compounds *trans*-**BBI-4Cl**·$(DMF)_2$, *cis*-**BBI-4Cl**·$(DMF)_2$ and **BBI-4Br**·$(DMF)_2$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet) +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2014.01.019.

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[16] Synthesis of **BBI-4Cl**: A 50 mL round-bottom flask was flame-dried under reduced pressure, and then biphenyl-3,3′,4,4′-tetraamine (0.21 g, 1.0 mmol), 3,5-dichloro-2-hydroxybenzaldehyde (0.42 g, 2.2 mmol), and ethanol (20 mL) were added under nitrogen. After 14 h' refluxing, yellow solid precipitated in the reaction mixture. The precipitate was filtered, washed with ethanol and chloroform, and then dried to obtain the product **BBI-4Cl** (0.34 g, 62%). M.p. > 300 °C. *Anal.* Calcd. for $[C_{26}H_{14}Cl_4N_4O_2]$: C, 56.14; H, 2.54; N, 10.07%. Found: C, 55.72; H, 3.02; N, 10.55%. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3418 (m), 2105 (w), 1640 (w), 1128 (vs), 615 (m). ^1H NMR (500 MHz, d^6-DMSO) δ: 8.12 (s, 2H, phenol), 7.88 (s, 2H, phenol), 7.64 (s, 2H, benzoimidazole), 7.63 (d, 2H, benzoimidazole), 7.54 (d, 2H, benzoimidazole). ESI-TOF-MS (m/z): Calcd. for $[C_{26}H_{14}Cl_4N_4O_2]^+$ 556.2, found 555.6. Synthesis of **BBI-4Br**: The synthesis of **BBI-4Br** was similar to that described for **BBI-4Cl**. Yield, 0.41 g, 56%. M.p. > 300 °C. *Anal.* Calcd. for $[C_{26}H_{14}Br_4N_4O_2]$: C, 42.54; H, 1.92; N, 7.63%. Found: C, 42.08; H, 2.40; N, 8.01%. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3386 (m), 2927 (m), 2360 (m), 1660 (m), 1455 (s), 1256 (m), 800 (m), 683 (m). ^1H NMR (500 MHz, d^6-DMSO) δ: 8.35 (s, 2H, phenol), 7.95 (s, 2H, phenol), 7.92 (s, 2H, benzoimidazole), 7.80 (d, 2H, benzoimidazole), 7.74 (d, 2H, benzoimidazole). ESI-TOF-MS (m/z): Calcd. for $[C_{26}H_{14}Br_4N_4O_2]^+$ 734.0, found 733.1.
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[18] Three single-crystal samples were covered with glue and mounted on glass fibers for data collection at 291(2) K with Mo-*K*α radiation (λ = 0.71073 Å) and a Bruker SMART 1 K diffractometer equipped with a CCD camera. Data collection was performed by using the SMART program, and cell refinement and data reduction were made with the SAINT program. The structures were solved by direct methods and refined by least-squares methods on Fo^2 by using the SHELXTL software package. *trans*-**BBI-4Cl**·$(DMF)_2$, $C_{26}H_{14}Cl_4N_4O_2\cdot(C_3H_7NO)_2$, Mr = 702.40, triclinic space group $P\bar{1}$, a = 8.059(2), b = 9.181(3), c = 11.255(3) Å, α = 78.189(4), β = 82.367(4), γ = 83.072(4)°, V = 804.1(4) Å^3, Z = 1, D_c = 1.451 g·cm^{-3}, crystal size (mm) = 0.06 × 0.08 × 0.16, 4036 reflections measured, 2785 unique (R_{int} = 0.052), S = 0.82, R_1 = 0.0512 and wR_2 = 0.1372; *cis*-**BBI-4Cl**·$(DMF)_2$, $C_{26}H_{14}Cl_4N_4O_2\cdot(C_3H_7NO)_2$, Mr = 702.40, triclinic space group $P\bar{1}$, a = 10.2554(10), b = 12.1015(12), c = 13.8172(13) Å, α = 85.911(2), β = 71.909(1), γ = 79.359(1)°, V = 1601.8(3) Å^3, Z = 2, D_c = 1.456 g·cm^{-3}, crystal size (mm) = 0.12 × 0.14 × 0.16, 8183 reflections measured, 5576 unique (R_{int} = 0.032), S = 0.83, R_1 = 0.0472 and wR_2 = 0.1225. *cis*-**BBI-4Br**·$(DMF)_2$, $C_{26}H_{14}Br_4N_4O_2\cdot(C_3H_7NO)_2$, Mr = 880.20, triclinic space group $P\bar{1}$, a = 10.3067(16), b = 12.3701(19), c = 13.878(2) Å, α = 85.703(2), β = 72.457(2), γ = 78.861(2)°, V = 1655.0(4) Å^3, Z = 2, D_c = 1.766 g·cm^{-3}, crystal size (mm) = 0.10 × 0.12 × 0.14, 8335 reflections measured, 5738 unique (R_{int} = 0.056), S = 0.78, R_1 = 0.0433 and wR_2 = 0.0988. Selected bond distances and bond angles are given in Table SI1. Moreover, intermolecular N–H···O and C–H···O hydrogen bonding interactions are given in Table SI2.

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