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STRUCTURAL AND QUANTUM CHEMICAL ANALYSIS ON
4,4′-DI(2-HYDROXYBENZYLAMINO)DIPHENYLMETHANE

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The title compound is analyzed by X-ray diffraction. ONIOM(B3LYP/6-31G(d,p):PM3) is used to investigate the optimized calculation and the frequency analysis of the molecule, in which the PM3 method was used for carbon and hydrogen atoms of the benzene ring and the B3LYP/6-31G(d,p) method was used for the other parts. Energy changes in the molecule are numerically investigated by the flexible scan at PM3 level. The nature of intramolecular interactions that stabilize the structure in vacuo and solid is studied. The results reveal that the molecule is flexible and molecular conformations can easily be mutually transformed through very small potential barriers.

K e y w o r d s: 4,4′-di(2-hydroxybenzylamino)diphenylmethane, crystal structure, quantum chemistry, ONIOM method.

Supramolecular chemistry refers to the area of chemistry that considers the self-assembly of two or more chemical species held together by non-covalent bonding interactions. It covers analytical, inorganic, organic, and physical chemistry as well as the other related disciplines, such as biology, material sciences, and catalysis. It has become a rapidly developing area in the last decades [1, 2]. Typically, fields of interest include researches on crystal engineering, molecular devices, molecular machinery, biomimetic chemistry, molecular recognition, selective separation, and host—guest chemistry. traditional chemistry focuses on the covalent bond, whereas supramolecular chemistry considers weaker and reversible non-covalent interactions that include hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π—π interactions and electrostatic effects. In a host-guest system, sufficiently large stacking space and as much as possible binding sites are necessary for a compound to be a host. In other words, the structural topology and binding relationship of a host molecule should be uniquely complementary to its guest. Hosts with the above-mentioned characteristics had shown that they were able to exhibit molecular recognition and form a complex with an appropriate guest. For instance, 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol, as the host, can selectively and effectively isolate 4-allylanisole from the crude volatile oil of *Zanthoxylum schinifolium* Sieb.et Zucc [3]; chiral hosts of amino acid type exhibit the chiral recognition ability towards organic enantiomers [4]; and *trans*-9,10-di(1′-naphthy1)-phenanthrene-9,10-diol can include many types of nitrogen-containing guests [5]. Note that the Schiff base of 4,4′-diaminodiphenylmethane, which has the structural features similar to those of the above-mentioned hosts, has widely been employed to generate novel supramolecular frameworks [6—9]. However, the study of its reduced product has not been reported in details. As the reduced product from the Schiff base, 4,4′-di(2-hydroxybenzylamino)diphenylmethane is one of interesting molecules because it has rigid phenyl rings and flexible methylene along with imino and hydroxyl groups that can form hydrogen bonds, while phenyl rings can partici-

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pate in π—π stacking. This work started from the characterization of the crystal structure by X-ray diffraction analysis. Moreover, parallel to the experimental investigation, molecular modeling and related quantum chemistry structural analysis techniques were used to help to understand the tendency in its interaction and mode.

EXPERIMENTAL

Well-shaped crystals of 4,4′-di(2-hydroxybenzylamino)diphenylmethane were obtained from ethanol solution.

Structure determination. Diffraction data was measured on a Bruker SMART CCD diffracto-meter at room-temperature (293(2) K) using graphite mono-chromated MoK_α radiation ($\lambda = 0.71073$ Å). The scan angle was $2.64 \leq \theta \leq 24.66°$. In total, 12104 reflections were collected, whereas 4271 of them were independent and 2931 of them were with $I \geq 2\sigma$. Using the SHELX-97 programs, all structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were added geometrically and refined using the riding model. Crystals of the title compound were colour-less, transparent, monoclinic, $P2_1n$ space group with the cell parameters: $a = 5.7991(7)$ Å, $b = 43.852(5)$ Å, $c = 8.5227(9)$ Å, $\beta = 91.909°$, $V = 2166.1(4)$ Å^3, $d_x = 1.259$ g/cm^3, $Z = 4$, $\mu = 0.080$ mm^{-1}, $F(000) = 872$. Final values of divergence factors were $R = 0.0598$, $wR = 0.1179$ [$w = 1/[\sigma^2(F_0^2) + (0.047P)^2 + 0.4544P]$, $P = (F_0^2 + F_c^2)/3$], $S = 1.056$, $(\Delta\rho)_{min} = -0.150$ e/Å^3 and $(\Delta\rho)_{max} = 0.036$ e/Å^3. The CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 701098, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

Calculation method. The optimized calculation and frequency analysis of the molecule were car-ried out by the ONIOM(B3LYP/6-31G(d,p):PM3) calculation. The PM3 method was used for carbon and hydrogen atoms of the benzene ring, and the B3LYP/6-31G(d,p) method was used for the other parts. The molecule was calculated by flexible scan on PM3 level when the energy change was inves-tigated. All calculations were based on the Gaussian03 program.

RESULTS AND DISCUSSIONS

Molecular and crystal structure of the title compound. Selected bond distances and angles of the title compound are given in Table 1, and hydrogen bonds are listed in Table 2. The bond distances and angles of the compound were in the normal range. The molecular structure is shown in Fig. 1. Al-though the C(14) atom is in the intermediate position, arranging some groups on both sides, the whole molecule is not mirror symmetrical to the C(14), H(14A), H(14B) plane. The dihedral angle between contiguous phenyl rings is 59.9°. The dihedral angle between the C(15),C(14),C(11)-containing plane and the C(14),C(11),C(12)-containing plane is 48.0°; the dihedral angle between the C(21),N(2),C(18)-containing plane and the N(2),C(18),C(17)-containing plane is 17.8°; the dihedral angle between the C(7),N(1),C(8)-containing plane and the N(1),C(8),C(9)-containing plane is 29.8°. All dihedral angles indicate that the molecule is rather flexible. However, on the other hand, the nitro-gen atom in the title compound forms the intramolecular O—H···N hydrogen bond with the adjacent hydroxyl group [O(1)···N(1) 2.630(2) Å, O(1)—H(1B)···N(1) 151(3)°; O(2)···N(2) (symmetry code: 1/2+x, 1/2–y, –1/2+z) 2.705(2) Å, O(2)—H(2B)···N(2) 153(3)°]. Thus, two six-membered (1),C(7),C(6),C(1),O(1),H(1B) and N(2),C(21),C(22),C(27),O(2),H(2B) benzo-heterocycles formed with increasing rigidity. The intermolecular N(1)—H(1A)···O(2) (symmetry code: –1/2+x, 1/2–y, –1/2+z) and N(2)—H(2A)···O(1) hydrogen bonds link each molecule with the other four (Fig. 2, *a*) to form a three-dimensional supramolecular network. An additional one-dimensional zigzag-like chain of C—H···π interactions {interatomic distance D$_{atm}$ [10]: H(14A)···C(16) (symmetry code: 1/2+x, 1/2–y, –1/2+z) 2.78 Å} make the network more stable (Fig. 2, *b*). The intermolecular hydrogen bonds and the C—H···π interaction result in the conformational differences between the experimentally de-

The selected bond lengths (Å) *and bond angle* (deg.) *for the title compound*

O(1)—C(1)	1.377(2)	C(1)—C(2)	1.378(3)	C(6)—C(5)	1.380(3)
N(1)—C(8)	1.416(3)	C(1)—C(6)	1.390(3)	C(6)—C(7)	1.505(3)
N(1)—C(7)	1.472(3)	O(2)—C(27)	1.375(3)	C(17)—C(16)	1.389(3)
N(2)—C(18)	1.408(3)	C(18)—C(17)	1.382(3)	C(8)—C(9)	1.384(3)
N(2)—C(21)	1.460(3)	C(18)—C(19)	1.396(3)	C(27)—C(26)	1.386(3)
C(13)—C(12)	1.386(3)	C(15)—C(16)	1.380(3)	C(23)—C(24)	1.375(3)
C(11)—C(10)	1.373(3)	C(15)—C(20)	1.390(3)	C(2)—C(3)	1.379(3)
C(11)—C(12)	1.393(3)	C(15)—C(14)	1.514(3)	C(26)—C(25)	1.385(4)
C(11)—C(14)	1.512(3)	C(13)—C(8)	1.385(3)	C(5)—C(4)	1.385(3)
C(19)—C(20)	1.376(3)	C(10)—C(9)	1.380(3)	C(22)—C(21)	1.509(3)
C(22)—C(27)	1.386(3)	C(22)—C(23)	1.378(3)	C(25)—C(24)	1.377(4)
C(3)—C(4)	1.372(3)				

C(8)—N(1)—C(7)	119.24(18)	C(19)—C(18)—N(2)	118.63(18)	C(5)—C(6)—C(7)	121.9(2)
C(18)—N(2)—C(21)	120.53(18)	C(16)—C(15)—C(20)	116.8(2)	C(1)—C(6)—C(7)	120.57(19)
O(1)—C(1)—C(2)	118.7(2)	C(16)—C(15)—C(14)	122.83(19)	C(19)—C(20)—C(15)	121.5(2)
O(1)—C(1)—C(6)	119.84(19)	C(20)—C(15)—C(14)	120.14(19)	C(18)—C(17)—C(16)	120.3(2)
C(2)—C(1)—C(6)	121.5(2)	C(8)—C(13)—C(12)	120.8(2)	C(9)—C(8)—C(13)	117.94(19)
C(17)—C(18)—C(19)	117.6(2)	C(10)—C(11)—C(12)	117.0(2)	C(9)—C(8)—N(1)	122.05(19)
C(17)—C(18)—N(2)	123.7(2)	C(10)—C(11)—C(14)	119.9(2)	O(2)—C(27)—C(22)	119.7(2)
C(23)—C(22)—C(21)	122.6(2)	C(12)—C(11)—C(14)	123.1(2)	O(2)—C(27)—C(26)	119.4(2)
C(27)—C(22)—C(21)	119.0(2)	C(20)—C(19)—C(18)	121.25(19)	C(22)—C(27)—C(26)	121.0(2)
C(13)—C(12)—C(11)	121.3(2)	C(11)—C(10)—C(9)	122.3(2)	C(15)—C(16)—C(17)	122.3(2)
C(5)—C(6)—C(1)	117.4(2)	C(23)—C(22)—C(27)	118.4(2)	C(11)—C(14)—C(15)	118.10(19)
C(13)—C(8)—N(1)	119.94(19)	N(1)—C(7)—C(6)	110.96(19)	C(10)—C(9)—C(8)	120.7(2)
C(24)—C(23)—C(22)	121.5(2)	C(1)—C(2)—C(3)	119.6(2)	N(2)—C(21)—C(22)	109.67(18)
C(6)—C(5)—C(4)	121.9(2)	C(25)—C(26)—C(27)	119.2(2)	C(24)—C(25)—C(26)	120.2(2)
C(3)—C(4)—C(5)	119.3(2)	C(23)—C(24)—C(25)	119.6(3)	C(4)—C(3)—C(2)	120.3(2)

termined molecular structure and the one calculated in vacuo. The related calculation and analysis are given in the next part.

Quantum chemistry structural analysis. The geometry of the molecule was fully optimized by the ONIOM (B3LYP/6-31G(*d*,*p*):PM3) method. In the optimized molecule, the two middle benzene rings are in the plane called P1 composed of C(14)H(14A)H(14B) as a mirror symmetry plane, and so are the other atoms except oxygen ones. Moreover, the farthest benzene rings were almost in the same plane. The N and H_O (H on oxygen) atoms were hydrogen bonded. The calculations showed the N(2)···H(2B) and N(1)···H(1B) bond lengths to be 1.916 Å and 1.917 Å respectively. In this way, two

Hydrogen bond lengths (Å) *and bond angles* (deg.) *for the title compound*

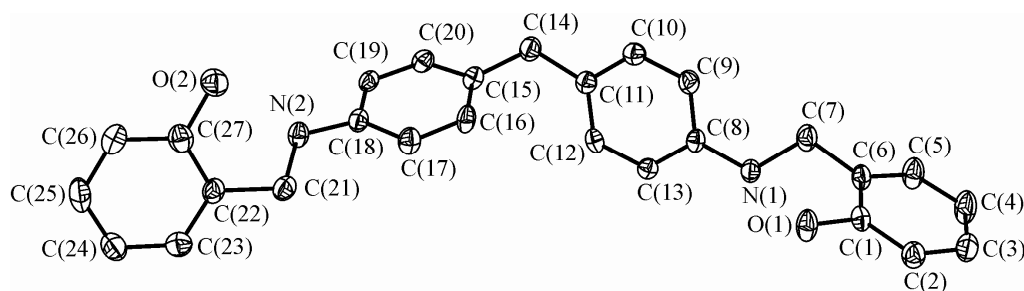| D—H···A	d(D—H), Å	d(H···A), Å	d(D···A), Å	∠DHA, deg.
N(1)—H(1A)···O(2) [–1/2+x, 1/2–y, –1/2+z]	0.91(2)	2.01(2)	2.910(2)	172(2)
O(1)—H(1B)···N(1)	0.93(3)	1.78(3)	2.630(2)	151(3)
N(2)—H(2A)···O(1)	0.91(2)	2.03(2)	2.937(2)	175(2)
O(2)—H(2B)···N(2) [1/2+x, 1/2–y, –1/2+z]	1.04(3)	1.74(3)	2.705(2)	153(3)

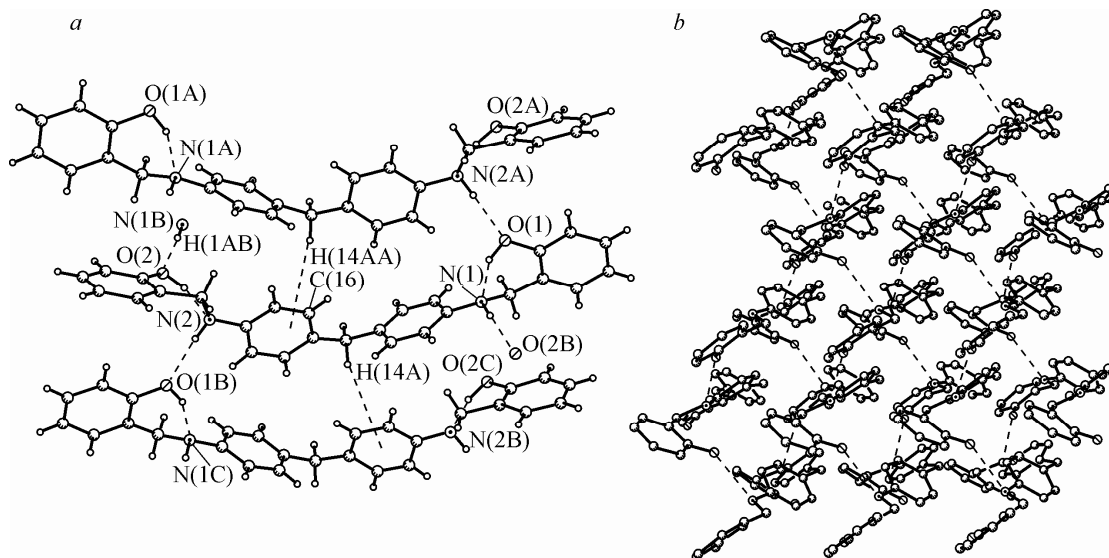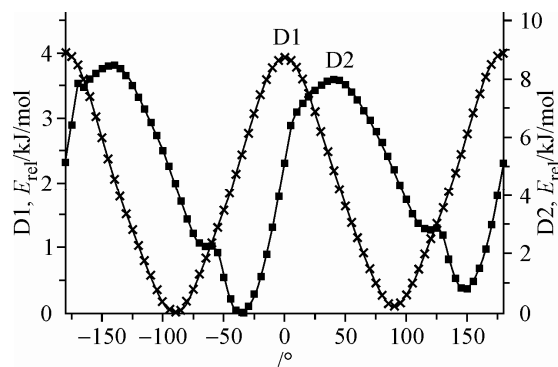Fig. 1. Molecular crystal structure of the title compound (hydrogen atoms are omitted for clarity)

Fig. 2. (a) Intra- and intermolecular hydrogen bonds and C—H···π interactions (indicated as dashed lines);
(b) stacking of the title compound along the y-axis

benzo nitrogen-oxygen heterocycles formed so that it made the molecule rigid and more stable as compared to the situation in which the hydrogen bond was absent. Single point energy of this molecule was calculated to be –384.894415 a.u. (–1010540.29 kJ/mol).

Energy change with different tropisms of benzene. In the optimized molecule, the dihedral angle made by the C(15)C(14)C(11) and C(14)C(11)C(12) planes was –88.5°; it was marked as D1. The energy of this geometry calculated at PM3 level was 0.00 kJ/mol. Then, using the PM3 method, the energy vs the D1 change was flexibly scanned with a step of 5° in the range between –180°and 180°during the structural optimization and energy calculation of the molecule. Thus, the tropism of

middle benzene would change continuously. Fig. 3 shows that there is a potential energy surface minimum when D1 is at –90.0 or 90.0°. The optimized molecule has high geometrical symmetry, so the energies are little changed when the molecule is reversed by 180°. The energies were calculated to be 0.00 kJ/mol and 0.10 kJ/mol respectively. As discussed above, the former geometry was highly sym-

Fig. 3. Curves of the different conformations of D1 and D2 with the corresponding energy

metrical, which made it more stable, so it had a lower energy. On the contrary, when D1 is 0.0 or 180.0°, there is a maximum on the potential energy surface, which was calculated to be 3.93 kJ/mol or 3.40 kJ/mol respectively. As compared to the above geometries when D1 is –90.0 or 90.0°, it resulted in more unstable geometries because the symmetry destroyed, equilibrium of atoms broke, and steric repulsion forces between two benzenes increased. Thus, there should be a maximum on the potential energy surface.

Different tropisms of the benzo nitrogen-oxygen heterocycle and the corresponding energy. In the optimized molecule, the dihedral angle made by C(21)N(2)C(18) and N(2)C(18)C(17) planes was –33.7°; it is was marked as D2. To locate the stationary points, the potential energy surface (PES) of the reactant system was scanned with respect to the significant geometry parameters D2 in the range between –180 and 180° using the PM3 method during the structural optimization and energy calculation of the molecule. Thus, tropisms of middle benzene would change continuously. A point on the scan curve corresponded to a geometry optimized with respect to all parameters except the scan coordinate. Fig. 3 also shows that there was a PES minimum when D2 was –33.7 or –150°. The optimized geometry was highly symmetrical, so the energy was little changed when it was reversed by 180°. The energies were calculated to be 0.00 kJ/mol and 0.83 kJ/mol respectively. As discussed above, the former geometry was highly symmetrical, which made it more stable. Also, benzenes on the same side had a vertical relation, which made steric hindrance lower in the molecule. Therefore, the former molecule had a low energy, and so did the latter. On the contrary, when D2 was –140.0 or 140.0°, there was a PES maximum, which was calculated to be 8.46 kJ/mol and 8.00 kJ/mol respectively. Similarly, as compared to the above geometries, when D2 was –33.7 or –150°, it resulted in unstable corresponding geometries because the symmetry destroyed, equilibrium of atoms broke, and steric repulsion forces between two benzenes increased. Thus, there would be a PES maximum. From the passage, we found that the largest energy difference between the minima and maxima was 3.93 kJ/mol when D1 varied from –180° to 180°. The corresponding geometries of different tropisms of middle benzenes could mutually converse experiencing an extremely small potential barrier. Likewise, the largest energy difference in the minima and maxima was 8.46 kJ/mol when D2 varied from –180° to 180°. The corresponding geometries of different tropisms of the benzo nitrogen-oxygen heterocycle could mutually converse undergoing an extremely small potential barrier. An analysis of the result revealed that the molecule was flexible and molecular conformations occurred easily because of a very small potential barrier.

Energy of the hydrogen bond and C—H···π. There are two intramolecular hydrogen bonds, one intermolecular hydrogen bond, and one intermolecular C—H···π interaction in the title compounds in crystal. However, there are only two intramolecular hydrogen bonds in the optimized structure in vacuo. In order to study the nature of the intramolecular interactions that stabilize the structure, so as to understand how the intermolecular interactions in crystal can modify the molecular structure, appropriate models have been chosen for calculations. The calculations were carried at the B3LYP/6-31++G(d,p) level using density functional theory. The result is shown in Table 3.

T a b l e 3

Interaction energies of the optimized conformation in vacuo and in crystal

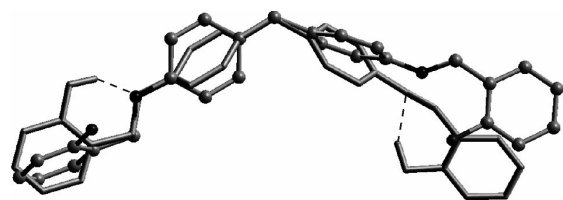| Interaction types		E, kJ/mol	
		Conformation in crystal	Conformation in vacuo
Intramolecular hydrogen bond	O(1)—H(1B)···N(1)	14.86	25.03
	O(2)—H(2B)···N(2)	25.90	25.00
Intermolecular hydrogen bond	N(1)—H(1A)···O(2)	13.79	
C—H···π interaction	C(14)H(14B)···H(16)C(16)	–1.64	
Sum of interactions		52.91	50.03

Fig. 4. Comparison of the optimized conformation and factual (ball-stick) conformation

In vacuo, the interaction energies of the two hydrogen bond energies in the molecule had little differences. But in crystal, they had a difference value of 11.04 kJ/mol. Interestingly, we found that the values of O(2)—H(2B)···N(2) both in vacuo and crystal were nearly the same, which can indirectly explain why benzo-heterocycles of N(2),C(21),C(22),C(27),O(2),H(2B) were in relatively better agreement.

In crystal, the intermolecular hydrogen bond energy of N(1)—H(1A)···O(2) was 13.79 kJ/mol. Due to the presence of the intermolecular hydrogen bond, the related groups are attracted to each other, especially six-membered benzo-heterocycles. This can help to understand why the benzo-heterocycle had a different tropism characterized by D2 in crystal and in vacuo.

The C—H···π energy between C(14)H(14B) and the benzene ring containing C(16)H(16) was calculated to be –1.64 kJ/mol. As a kind of a short contact displaying a repulsive force, the C—H···π interaction leads to the tropism change in the middle benzene ring characterized by D1 in crystal. Under the combined action of the inter-molecular hydrogen bond and C—H···π interactions, the benzo-heterocycles and middle benzene deviated to a certain degree characterized by the enlargements of D1 and D2 in solid, which was the main reason why the optimized conformation in vacuo and crystal can not be in good agreement.

CONCLUSIONS

The title compound was synthesized from the reduction of bis(salicylidene)-4,4′-diaminodiphenylmethane and characterized. Then the quantum chemistry structural analysis was used to investigate the structural topology and molecular conformations.

Based on ONIOM(B3LYP/6-31G(d,p):PM3) calculations, the molecule configuration presented the symmetry distribution by the plane of H(14A), H(14B), C(14), and showed a certain degree of deviation to the configuration of the practical crystal data. Comparing the optimized and the factual conformations (Fig. 4), one may clearly see that, apart from a few atoms such as C(14),C(15), and N(2) in good agreement, there is a significant difference between the two dihedral angles of the molecule. The dihedral angle made by the C(15)C(14)C(11) and C(14)C(11)C(12) planes was –88.5° for the calculated structure D1,but it was 48° for the crystal. The dihedral angle made of the C(21)N(2)C(18) and N(2)C(18)C(17) planes was –33.7° for the calculated structure D2, but it was 17.8° for the crystal. The reason of such a large deviation could be that the theoretical configuration was calculated in accordance with the vacuum conditions, and the crystal data was the molecular conformation in the crystal condition. When molecules are accumulated into the crystal, even though some of the reverse dihedral angle would result in an increase in the molecular internal energy, because of the molecular flexibility this energy increase can be easily compensated by the energy of the crystal lattice formation and intermolecular forces.

Furthermore, when D1 or D2 changed, the largest energy differences between the minima and maxima were calculated to be 3.93 kJ/mol and 8.46 kJ/mol respectively. The corresponding geometries of different tropisms of middle benzenes or the benzo nitrogen-oxygen heterocycle could mutually converse undergoing an extremely small potential barrier. The hydrogen bond energy was about 8.4—42 kJ/mol. This means that when 1 mol of the hydrogen bond forms in 1 mol of the molecule, it can release the energy of 8.4 kJ. For the title compound, this energy can easily support D1 and D2 ranging from –180 to 180°.

All above discussions could also account for the reason why, in the course of supramolecular host-guest structure formation, the conformation transition of the title compound could occur easily to fit the topology of guest molecules.

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